PB-216 605

CALCIUM PHOSPHATE PRECIPITATION IN WASTEWATER TREATMENT

Arnold B. Menar, et al

California University

Prepared for:

National Environmental Research Center

December 1972

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151

W73-06038

EPA-R2-72-064
DECEMBER 1972

Environmental Protection Technology Series

PB 216 605

Calcium Phosphate Precipitation in Wastewater Treatment

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. Department of Commerce
Springfield VA 22151

Office of Research and Monitoring

U.S. Environmental Protection Agency

Washington, D.C. 20460

IRV

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Monitoring, Environmental Protection Agency, have been grouped into five series. These five broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The five series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies

This report has been assigned to the ENVIRONMENTAL PROTECTION TECHNOLOGY series. This series describes research performed to develop and demonstrate instrumentation, equipment and methodology to repair or prevent environmental degradation from point and non-point sources of pollution. This work provides the new or improved technology required for the control and treatment of pollution sources to meet environmental quality standards.

SELECTED WATER RESOURCES ABSTRACTS INPUT TRANSACTION FORM	W

CALCIUM PHOSPHATE PRECIPITATION IN WASTEWATER TREATMENT,

Menar, A. B. and Jenkins, D.

EPA Region 17080 DAR

Environmental Protection Agency, ~~Washington, D.C.~~ Cincinnati, Ohio, ~~Office of Research and Monitoring~~ National Environmental Research Center. ~~EPA-R2-72-064~~

Environmental Protection Agency Technology Series Report ~~No.~~ EPA-R2-72-064, ~~96 p.~~ December, 1972. 25 fig, 15 tab, 48 ref.

~~This report examined the~~ precipitation of calcium phosphate from both synthetically derived wastewater and from actual wastewater. An amorphous tricalcium phosphate was the steady state solid phase that controlled dissolved phosphate residual. The solubility of this phase determined from chemically defined systems was used with success to predict dissolved phosphate residuals from both chemically defined systems and actual wastewaters. Suspension settling was enhanced by magnesium hydroxide precipitation but not by calcium carbonate precipitation. In wastewater of moderate alkalinity and hardness, a phosphate removal in excess of 80% was consistently achieved at pH 9.5 with lime doses of , at the most, 200 mg/l as calcium carbonate. The overall phosphate removal performance was dictated by the performance of the precipitation reactor and its insuing sedimentation basin. Phosphate containing particles that escaped sedimentation could not be removed by filtration because they dissolved rapidly during the recarbonation process that necessarily precedes the filtration step. (Smith-Texas)

*Chemical precipitation, *Waste water treatment, *Phosphates, Chemical reactions, Filtration, Sedimentation, Separation techniques, Treatment facilities, Water pollution control, Water quality control, Sedimentation, Calcium carbonate, Calcite, Settling basin

*Tricalcium phosphate

05D

Copy available from GPO $0.25 Dec ... from NTIS as PB- ... $3.00.

Send To:
WATER RESOURCES SCIENTIFIC INFORMATION CENTER
U.S. DEPARTMENT OF THE INTERIOR
WASHINGTON D.C. 20240

Richard M. Smith, Jr. | Texas Univ, Austin

EPA-R2-72-064
December 1972

CALCIUM PHOSPHATE PRECIPITATION IN WASTEWATER TREATMENT

by

A. B. Menar
D. Jenkins

Grant #17080 DAR

Project Officer

Warren A. Schwartz
U.S. Environmental Protection Agency
National Environmental Research Center
Cincinnati, Ohio 45268

for the

OFFICE OF RESEARCH AND MONITORING
U.S. ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402 - Price $1.50

EPA Review Notice

This report has been reviewed by the Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

ABSTRACT

This investigation examined the precipitation of calcium phosphate both from chemically-defined solutions representative of wastewater composition and from wastewater. The steady state solid phase that controlled dissolved phosphate residual was an amorphous tricalcium phosphate. The solubility of this phase, determined from chemically-defined systems, was used with success to predict dissolved phosphate residuals from both chemically-defined systems and wastewaters. Suspension recycle was found to result in lower dissolved phosphate residuals, but poor suspension settling below pH 10 made this process difficult to maintain. Suspension settling was enhanced by $Mg(OH)_2$ precipitation but not by $CaCO_3$ precipitation. In wastewater of moderate alkalinity and hardness, a phosphate removal in excess of 80% was consistently achieved at pH 9.5 with lime doses of, at the most, 200 mg/ℓ as $CaCO_3$. The overall phosphate removal performance was dictated by the performance of the precipitation reactor and its ensuing sedimentation basin. Phosphate-containing particles that escaped sedimentation could not be removed by filtration because they dissolved rapidly during the recarbonation process that necessarily precedes the filtration step.

This report was submitted in fulfillment of Project Number 17080 DAR under the sponsorship of the Environmental Protection Agency by the Sanitary Engineering Research Laboratory, University of California, Berkeley, California 94720.

CONTENTS

Section		Page
I	Conclusions	1
II	Recommendations	5
III	Introduction	7
IV	Phosphate Removal from Wastewaters by Calcium Phosphate Precipitation	9
V	Mechanism of Calcium Phosphate Precipitation	15
VI	Approach Rationale	21
VII	Experimental Equipment and Procedures	23
VIII	Precipitation of Calcium Phosphate in Chemically-Defined Systems	31
IX	Precipitation of Phosphate in Wastewater	57
X	Acknowledgments	71
XI	References	73
XII	Glossary	77
XIII	Appendices	79

Preceding page blank

FIGURES

		Page
1	Lime Requirement to Reach pH 11 as a Function of Wastewater Alkalinity	10
2	Schematic Flowsheet for Experiments on Chemically-Defined Systems	24
3	Schematic of Calcium Phosphate Precipitation with Suspension Recycle	25
4	Treatment Systems Used in Studies at SEPL Pilot Plant	27
5	Dependence of Steady State P_T Concentration on Solution Composition and pH in Batch Reactors	33
6	Dependence of Steady State P_T Concentration on Detention Time in CSTR Experiments	34
7	Effect of pH on pA for Various Calcium Phosphate Solids	36
8	Effect of pH on pA of Tricalcium Phosphate	37
9	Critical Ionic Concentrations in Batch and CSTR Experiments	38
10	Effect of Mg on pA $Ca_3(PO_4)_2$	40
11	Influence of Mg on Steady State Concentrations of Ca, Mg, C_T, and P_T at pH 9.5	42
12	Effect of C_T on pA $Ca_3(PO_4)_2$	44
13	Effect of C_T on Steady State Concentrations of Ca, Mg, and P_T and on Amount of Precipitated Carbonate at pH 9.5	45
14	Effect of C_T on Steady State Concentrations of Ca, Mg, and P_T and on Amount of Precipitated Carbonate at pH 11.0	46
15	Effect of pH on Ca/P_T Mole Ratio of the Precipitate and on Carbonate Incorporation Into the Precipitate	47
16	Effect of Suspension Concentration on Effluent Phosphate Concentration in Precipitate Recycle Experiments	51

		Page
17	Steady State Ca and C_T Concentrations During Precipitate Recycle Experiments	53
18	Effect of Suspension Concentration on Rate of Calcium Phosphate Precipitation in Batch Experiments	54
19	Effect of Suspension Concentration on pA $Ca_3(PO_4)_2$ in Precipitate Recycle Experiments	55
20	Phosphorus Removal Performance of the Entire Process Train During Pilot Plant Runs on Wastewater	60
21	Comparison of Lime Slurry Addition to Dissolved Lime Concentration in Wastewater Experiments	62
22	Change in Dissolved Ca and P_T Concentrations in Reactor Compartments – Wastewater Experiments	63
23	Dependence of pA $Ca_3(PO_4)_2$ on pH for Wastewater Experiments	64
24	Settling Properties of Calcium Phosphate-Carbonate Suspensions (Series I)	67
25	Settling Properties of Calcium Phosphate-Carbonate Suspensions (Series II)	68
26	Critical Ionic Concentrations as Determined by Walton et al. and by This Investigation	84
27	Effect of Unit Processes on pH	90
28	Effect of Unit Processes on Total Phosphate Residuals (Runs 1, 2, and 3)	91
29	Effect of Unit Processes on Total Phosphate Residuals (Runs 4 and 5)	92
30	Effect of Unit Processes on Dissolved Phosphate Residuals (Runs 1 and 2)	92
31	Effect of Unit Processes on Dissolved Phosphate Residuals (Runs 3, 4, and 5)	93
32	Effect of Unit Processes on Dissolved Calcium Concentration (Runs 1, 2, and 3)	94
33	Effect of Unit Processes on Dissolved Calcium Concentration (Runs 4 and 5)	95
34	Effect of Unit Processes on Alkalinity	96

TABLES

		Page
1	Component Concentrations in Wastewater (From Ferguson [3])	21
2	Initial Composition of Batch Systems Used to Define Time to Reach Steady State	32
3	Initial Concentrations in CSTR Experiments to Determine Effect of Magnesium	41
4	Initial Conditions for CSTR Experiments to Determine Effect of Carbonate (C_T)	43
5	Initial Conditions for CSTR Experiments to Determine Effect of Carbonate on Phosphate and Other Component Residuals	43
6	Comparison of Predicted and Experimental Residual Phosphate Values in Chemically-Defined Systems	50
7	Comparison of Predicted and Experimental Residual Phosphate Values in Chemically-Defined Systems Corrected for Calcium Carbonate Precipitation	51
8	Operating Conditions and Results for Wastewater Experiment 1	58
9	Operating Conditions and Results for Wastewater Experiment 2	58
10	Operating Conditions and Results for Wastewater Experiment 3	59
11	Operating Conditions and Results for Wastewater Experiment 4	59
12	Operating Conditions and Results for Wastewater Experiment 5	60
13	Comparison of Predicted and Average Experimental Dissolved Phosphate Residuals for Wastewater Experiments	63
14	Initial Component Concentration for Precipitate Separation Experiments, Series I	66
15	Initial Component Concentration for Precipitate Separation Experiments, Series II	66

SECTION I

CONCLUSIONS

The general objective of this investigation was to develop a method of predicting the performance of phosphate removal processes that involve the precipitation of calcium phosphate. The development of this predictive method was based on a steady state precipitation model. The model was developed by conducting experiments in chemically-defined systems and then examining the utility of these results in predicting dissolved phosphate residuals obtained by precipitation of calcium phosphate from wastewaters.

It became evident as the work progressed that a major determining factor in the efficiency of calcium phosphate precipitation processes was the ability to separate the insolubilized phosphate. The objectives of the work were therefore expanded to include an examination of some of the chemical factors that influenced precipitate separation by sedimentation, and of some of the process considerations that determine the efficiency of particulate phosphate removal.

CHEMICALLY-DEFINED SYSTEMS

The effect of common wastewater components (calcium, carbonate, magnesium) and precipitation conditions (pH and reaction time) on dissolved phosphate residual was investigated in chemically-defined systems in both CSTR and batch reactors. At chemical component concentrations typical of wastewaters, steady state levels of dissolved phosphate were reached in continuous flow reactors after nominal residence times of 10 min and were maintained for at least 200 min – an average residence time range typical of wastewater precipitation processes.

The data from chemically-defined systems suggested that the nature of the steady state phase was one with the stoichiometric and solubility characteristics of tricalcium phosphate $Ca_3(PO_4)_2$(pA = 23.56). This solid was amorphous and did not have a distinct X-ray diffraction pattern. However, later calcium phosphate precipitation experiments in chemically-defined solutions in which precipitate recycle was conducted showed the presence of a solid with the X-ray diffraction pattern of tricalcium phosphate ($Ca_3(PO_4)_2 \cdot 4H_2O$). Using the solubility of tricalcium phosphate (pA = 23.56) to predict residual dissolved phosphate concentration in chemically-defined systems gave agreement within 25% of experimental values for systems in which the initial magnesium concentration was less than 2 mM (200 mg/L as $CaCO_3$) and the initial carbonate concentration was less than 4 mM (400 mg/L as $CaCO_3$) – neither of which is rarely exceeded in wastewaters.

The recycling of precipitate suspension in chemically-defined systems was found to enhance the removal of dissolved phosphate and therefore lower the phosphate residual for a given pH and solution composition. Difficulties were encountered, however, in these experiments because of poorly settling suspensions which resulted in the inability to maintain high suspension concentrations for long periods. Studies in the critical area of the settling properties of calcium phosphate–carbonate suspensions conducted in chemically-defined systems revealed that initial magnesium concentration and the pH of precipitation were the most important factors influencing the separation of these suspensions by sedimentation. Increases in the pH to between 9.0 and 11.0 improved the settling of the suspension. The beneficial influence of magnesium concentration on suspension settling was exerted most strongly at pH values of greater than 10.5 where precipitation of gelatinous $Mg(OH)_2$ was likely. Suggestions in the literature that calcium carbonate precipitation aids in precipitate separation by producing a dense suspension were not supported by this investigation.

In light of the stated findings it appears that high (>90%) phosphate removal by calcium phosphate precipitation followed by suspension settling is only possible at pH values of greater than 10. It would also appear that to achieve the same degree of phosphate removal at a pH of 9 to 10 the precipitate must be coagulated either by cationic polyelectrolytes, ferric chloride, or alum.

PHOSPHATE REMOVAL FROM WASTEWATERS

Investigations of phosphate removal from wastewaters by calcium phosphate precipitation were conducted at the Sanitary Engineering Research Laboratory (SERL) wastewater treatment facility. The phosphate removal performance of two treatment schemes was examined. The first involved primary sedimentation, activated sludge, lime precipitation, recarbonation, and clinoptilolite sorption; the second, lime precipitation following primary sedimentation.

Values of residual dissolved phosphate in wastewater precipitated with lime at pH values between 9.5 and 11.0 could be predicted to within 25% of their experimental values if these predictions were based on the initial concentrations of dissolved lime rather than on the total lime added and if a correction for calcium complexation was made. This was because the efficiency of lime dissolution in the slaking operation was poor and lime continued to dissolve throughout the several compartments of the precipitation unit.

An overall phosphate removal of greater than 80%, to achieve a residual of less than 2 mg P/ℓ, could be consistently achieved from this wastewater, which was one of average alkalinity (240 mg/ℓ as $CaCO_3$) and a typical Ca/Mg mole ratio of 3, by precipitating activated sludge effluent or primary effluent with lime doses of 200 mg/ℓ as $CaCO_3$ to achieve a pH of 9.5.

The overall phosphate removal performance of the entire treatment train was dictated by the combined performance of the precipitation reactor and the ensuing precipitate separator (in this case a sedimentation basin). Any calcium phosphate particles that escaped sedimentation were dissolved in the low average residence time (5 min) recarbonation basin that necessarily preceded the clinoptilolite sorption columns. This observation has important ramifications in the removal of phosphate by calcium phosphate precipitation. It means that improvement of the overall phosphate removal of a calcium phosphate precipitation process cannot be achieved by post-filtration of the effluent from the solids separator of such a process. Filtration of such an effluent will require a prior downward pH adjustment, but this pH adjustment will cause a rapid dissolution of calcium phosphate particles making it impossible to remove them by filtration. These observations emphasize the importance of solids separation in calcium phosphate removal and suggest this general topic as a fruitful area for investigation.

SECTION II

RECOMMENDATIONS

The work reported herein has demonstrated that short-term calcium phosphate precipitation processes can be modelled successfully on the basis of the formation of an amorphous tricalcium phosphate. Indications that this steady state solid phase can be made to transform and grow into a more insoluble calcium phosphate phase were obtained from precipitate recycle experiments. It is recommended that these experiments be further pursued to determine the factors that influence the formation and growth of more insoluble calcium phosphate solids in wastewaters since the formation of these solids will allow the attainment of lower dissolved phosphate residuals. Investigations of these phenomena should proceed along several lines including: 1) the role of recycled precipitate in providing crystal growth opportunity, 2) the role of precipitate in a sludge blanket clarifier in providing sites for crystal growth, and 3) the possible use of calcium phosphate clinker from lime regenerated by recalcining to provide material on which calcium phosphate crystal growth may occur.

An important conclusion of this investigation is that the phosphate residuals in effluents of calcium phosphate precipitation processes cannot be reduced by post-filtration because prior downward pH adjustment will dissolve the phosphate-containing particles. It is important therefore to devote considerable effort to improving precipitate removal by sedimentation processes, especially since it is possible to produce low dissolved phosphate residuals at pH values of 8.5 – 9.5 (but at these pH values precipitate separation is difficult). The factors that influence the flocculation and settling properties of calcium phosphate–carbonate suspensions produced at pH values below 10 should be investigated. Such an investigation should consider the surface properties of such suspensions and their possible modification by coagulants to improve their settling properties.

Preceding page blank

SECTION III

INTRODUCTION

PHOSPHATES IN WASTEWATERS

The conventional combination of primary sedimentation and secondary biological treatment processes with anaerobic digestion for sludge treatment can be relied upon to remove between 2 and 3 mg P/ℓ from domestic wastewater of average strength. With the current domestic wastewater total phosphate content averaging about 10 mg P/ℓ, such removals typically account for some 20% to 30% of the incoming phosphate in domestic wastewater. About half of the total phosphate in domestic sewage is derived from synthetic detergent builders so that even if the phosphates in these products were to be completely replaced by nonphosphate containing compounds, a sewage with some 5 mg P/ℓ would result. Treatment of such a wastewater by current primary and secondary treatment schemes would be expected to leave a residual of some 2 to 3 mg P/ℓ. In instances where phosphate has been identified as a nutrient limiting the growth of aquatic photosynthetic organisms it is generally agreed that growth control over these organisms by controlling phosphate concentration may only be exerted when phosphate levels on the order of 50 μg/ℓ or less are reached. It would therefore appear that in such instances treatment further than the conventional primary and secondary biological methods would be needed to produce such phosphate levels. Since complete elimination of phosphate from synthetic detergents is neither an impending nor a likely event and would not reduce raw sewage phosphate to less than 5 mg P/ℓ in any case, the development of processes that achieve high phosphate removals is justified.

Of the treatment processes suggested for increasing phosphate removal to a level greater than that possible by primary and secondary treatment, those using precipitation with metal ions are the only ones to have found wide application and to be economically feasible. Of the chemical precipitants commonly used (ferric and ferrous iron, aluminum and calcium salts) lime has been the most common, possibly because of a combination of its cheapness, the capability for its regeneration, and its familiarity in the field. Most calcium phosphate precipitation schemes involve raising the pH of the waste stream to 11 or higher. Under these conditions low phosphate residuals (<1 mg P/ℓ) and readily settleable suspensions (supposedly because of concomitant $Mg(OH)_2$ precipitation) are obtained. However, to achieve these high pH values on a variety of typical wastewaters Nesbitt [1] has reported that lime doses of between 280-720 mg/ℓ as $Ca(OH)_2$ are required since the lime dose is largely determined by the wastewater alkalinity. Moreover, pH adjustment of the treated effluent (commonly by recarbonation) is mandatory following these high pH precipitation processes.

Preceding page blank

Several authors (Menar and Jenkins [2], Ferguson [3], Ferguson et al. [4], and Jenkins et al. [5]) have suggested and demonstrated experimentally that phosphate residuals of 1 mg/ℓ or less can be obtained in wastewaters and synthetic systems representing wastewaters under some conditions at pH values far below 11. Most of these experiments have, however, been conducted in batch systems with reaction times and concentration ranges different from those that exist in a typical lime precipitation unit for removing phosphate from wastewater.

It was the purpose of this investigation to determine the behavior of chemically-defined systems representative of wastewater when subjected to phosphate precipitation by the addition of calcium salts (including lime) at various conditions of pH and under the physical constraints of reaction time and reactor design typical of a wastewater phosphate precipitation process. The overall aim of such experiments was to develop a predictive method that would allow the determination of chemical dose and phosphate residuals from chemically-defined systems and test it on wastewater.

OBJECTIVES

The general objective of this research was to develop a method for predicting the performance of phosphate precipitation processes involving the addition of calcium as a precipitant. Such processes include but are not necessarily restricted to: lime addition; the addition of calcium salts plus strong base; and the use of existing wastewater calcium hardness as a phosphate precipitant accompanied by aeration for upward pH adjustment. The general objective was reached by the fulfillment of the two following specific objectives: 1) the development of a predictive method based on calcium phosphate precipitation experiments in chemically-defined systems containing calcium, magnesium, orthophosphate, carbonate, hydrogen ion and water, and 2) the testing of the results of these experiments on domestic wastewaters under differing conditions of precipitation to determine the utility of the predictive method.

It became evident as the work progressed that a major determining factor in the efficiency of calcium phosphate precipitation processes was the ability to separate the insolubilized calcium phosphate. The objectives of the work were therefore expanded to include an examination of some of the chemical factors that influenced precipitate separation by sedimentation.

SECTION IV

PHOSPHATE REMOVAL FROM WASTEWATERS BY CALCIUM PHOSPHATE PRECIPITATION

The precipitation of calcium phosphate from wastewater has most commonly been conducted by the addition of unslaked or slaked lime to provide simultaneous increases in both calcium and hydroxyl ion. Most calcium phosphate precipitation schemes involve raising the pH of the waste stream to at least 10.5 (and often above pH 11) because in this pH range experience has shown that low dissolved phosphate residuals (<1 mg P/ℓ) are obtained together with a settleable precipitate.

Perhaps the earliest observation of the use of lime for phosphate precipitation in the waste treatment field was by Rudolfs [6]. He concluded that phosphate removals exceeding 90% – to reach residuals of approximately 0.3 mg P/ℓ – could be obtained together with excellent flocculation by lime addition to reach a pH of higher than 10.1.

Because phosphate precipitation processes using calcium have been conducted at high pH values, lime requirements have been largely dictated by the alkalinity of the wastewaters and have borne little or no relationship to its phosphate concentration. Thus Wuhrmann [7] states that the lime requirement for phosphate removal at pH 10.5 to 11 is equal to 1.5 times the carbonate hardness. Mulbarger *et al.* [8] and Buzzell and Sawyer [9] present a summary figure (Figure 1) of lime dose required to attain pH 11.0 as a function of wastewater alkalinity. The wide variation in lime doses to produce low dissolved phosphate residuals (0.4-2.4 mg P/ℓ) is indicated by Nesbitt's [1] summary of the literature in which it is revealed that doses ranging from 280 to 720 mg/ℓ $Ca(OH)_2$ were employed by various investigators.

From a survey of operating data in tertiary lime precipitation plants at Blue Plains, Washington, D. C.; Pomona, California; Lebanon, Ohio; Las Vegas, Nevada; and S. Lake Tahoe, California, Seiden and Patel [10] have concluded that residual dissolved phosphate concentration will be about 0.15 mg P/ℓ at pH 11. Notwithstanding the conclusion that high pH operation produces readily settleable precipitates, it is Nesbitt's opinion that a minimum phosphate residual can only be obtained if a filtration step (necessarily requiring recarbonation) follows lime

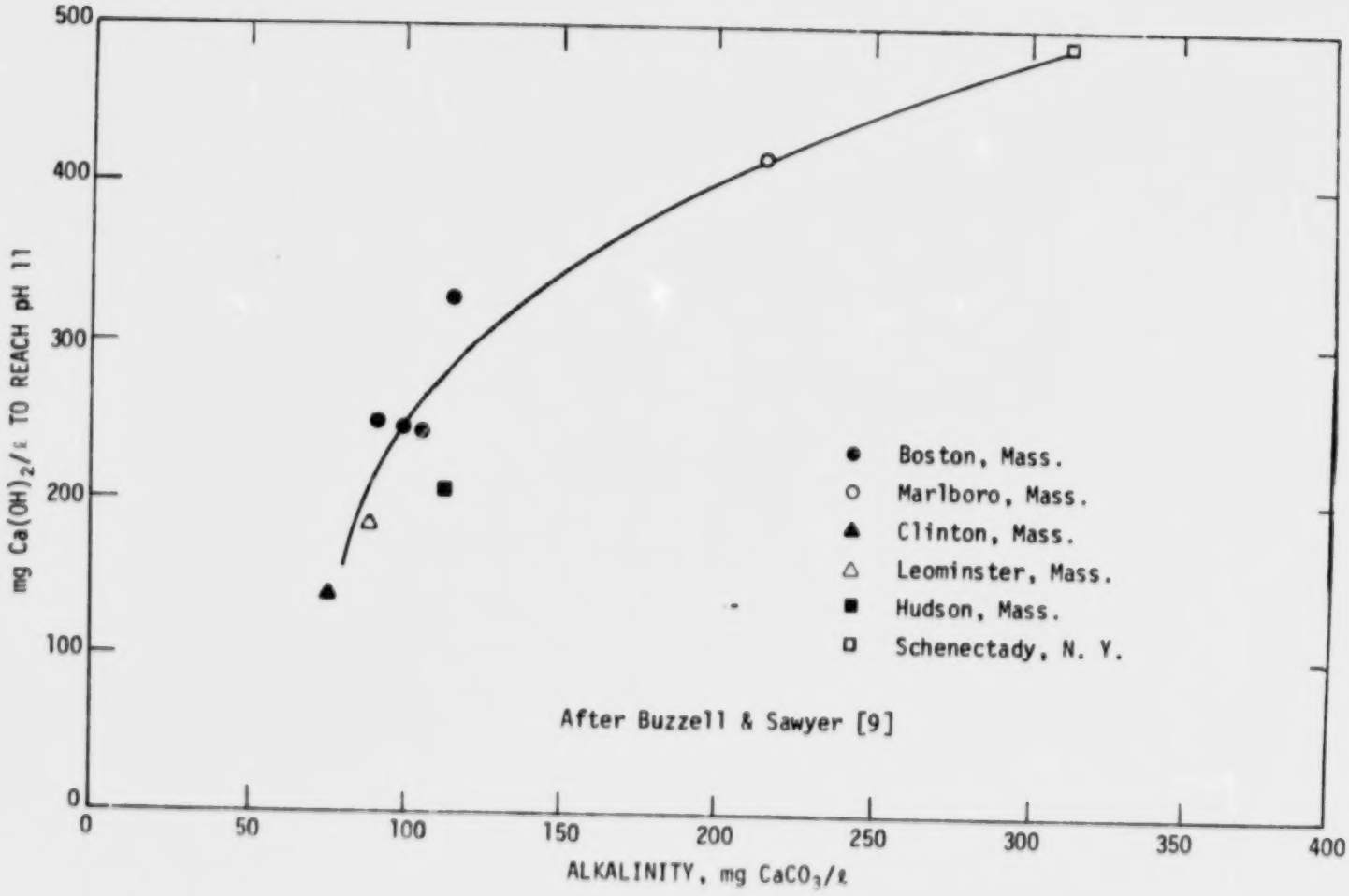


FIGURE 1. LIME REQUIREMENT TO REACH pH 11 AS A FUNCTION OF WASTEWATER ALKALINITY

precipitation. It is interesting, however, to note that if such a filtration step is contemplated for the removal of calcium phosphate particles from the effluent of a high pH precipitation unit it will be necessary to lower the pH value of the effluent (possibly by recarbonation) prior to filtration. The effect that the fall in pH has on the dissolution of calcium phosphate particles has not been discussed by authors who suggest filtration following lime precipitation to enhance phosphate removal.

Wuhrmann [7] has indicated that the calcium carbonate and apatite precipitates that form at high pH values do not settle readily, and he suggests the addition of 1 to 2 mg/ℓ Fe(III) to aid flocculation of the precipitates. In pilot plant post-precipitation or tertiary treatment of activated sludge effluent by this method (268 mg/ℓ $Ca(OH)_2$, 1 to 2 mg/ℓ Fe(III), pH 11.1) phosphate reductions from 3.2 to 0.4 mg P/ℓ were obtained. Results that indicate the carryover of phosphate in particles were obtained by Owen [11] who precipitated phosphate from a high-rate trickling filter effluent. Using 720 mg/ℓ $Ca(OH)_2$, a dissolved phosphate residual of 0.13 mg P/ℓ was obtained, while the total phosphate residual was 1.7 mg P/ℓ. Reducing the lime dose to 360 mg/ℓ produced a soluble phosphate residual of 1.5 mg P/ℓ and a total residual of 2.6 mg P/ℓ.

The use of alum and lime at pH of 10 to 11 has been reported by Spiegel and Forrest [12] at Amarillo, Texas, where the wastewater phosphate concentration was reduced to at least 0.4 mg P/ℓ.

Experience at the South Tahoe Public Utilities District Plant [13,14] has shown that the addition of 400 mg/ℓ CaO to activated sludge effluent to raise the pH to 11.5 will produce a phosphate residual of 0.3 mg P/ℓ by plain settling of the precipitate. However, the process flow sheet has included multimedia filtration subsequent to the sedimentation of the precipitate.

A *Densator* pilot plant operated at the Los Angeles County Sanitation District's Pomona facility for conditioning activated sludge effluent prior to treatment by ion exchange showed the beneficial effect of filtration in decreasing phosphate residuals [15]. When operated between pH 10 and 11 the *Densator* produced an effluent containing an average total phosphate of 1.85 mg P/ℓ and an orthophosphate of 0.2 mg P/ℓ. Filtration changed these values to 0.11 and 0.09 mg P/ℓ, respectively. Operation at pH values in the range 9.1 to 9.8 produced mean unfiltered residuals of 5.5 mg P/ℓ total phosphate and 0.86 mg P/ℓ orthophosphate, which were reduced to 0.65 and 0.48 mg P/ℓ by filtration.

In summary, high pH (>10.5) lime precipitation processes, therefore, appear to produce low residuals (0.5 mg P/ℓ), but separation of the colloidal precipitate may be difficult and require the use of coagulants.

There are several processes and suggested processes for calcium phosphate precipitation that involve the use of pH values lower than 10.5. In one

of these, the phosphate extraction process (PEP) proposed by Albertson and Sherwood [16], a key feature is the recycle of previously formed chemical sludge. The process involves lime addition to raw wastewater in a flocculator-clarifier to achieve a pH of 9.5 to 10.5, and recycle of clarifier underflow to maintain a solids concentration of 500 to 2000 mg/ℓ in the flocculator. The clarifier effluent which contains residual total phosphate of about 2 to 3 mg P/ℓ is fed to a completely mixed activated sludge aeration basin which further reduces the phosphate content to 1-2 mg P/ℓ and is claimed to provide an overall process BOD and suspended solids removal of 90% to 95%. Chemical sludge recovery by thickening, dewatering, combustion (calcining), and scrubbing is proposed. It is also proposed that pH adjustment following lime treatment to a range that is suitable for activated sludge operation can be achieved by the biologically produced CO_2 in the completely mixed aeration basin. This proposition is supported by studies at the South Tahoe Public Utilities District Plant [14] which indicate that when recalcined lime was added to the primary clarifier to produce a primary effluent of pH 11 the aeration basin contents some 5 ft into the aeration basin had a pH of 8.5 to 8.6.

Buzzell and Sawyer [9] expressed doubts that an activated sludge unit could be effectively operated on a primary effluent that has been treated with lime to a pH of 10 to 11 since insufficient degradable organic carbon would be present. In addition, it is possible that the precipitation unit might reduce phosphate concentrations to the point that the ensuing biological process would be phosphorus limited; it also is possible that carryover of solids from the flocculator process could significantly decrease the phosphate removal of the process. Humenick and Kaufman [17] have used the foregoing rationale to suggest that a chemical-biological process combination for achieving high BOD and phosphate removals should use a high-rate biological treatment prior to a chemical precipitation unit.

The recirculation of chemical sludge in the PEP process besides aiding the flocculation of wastewater particulates, enables total phosphate residuals of about 2 mg P/ℓ to be achieved at approximately one pH unit lower than without precipitate recycle and consequently with about one half the lime dose of a conventional lime precipitation process. The presence of recycle undoubtedly increases the rate of calcium phosphate precipitation by providing nuclei or growth sites for precipitate formation and growth. The provision of nuclei for the precipitation of apatite has been shown by Stumm and Leckie [18] and Ferguson et al. [4] to strongly influence the rate of phosphate removal under similar conditions in chemically-defined systems.

The significance of sludge recycle has been demonstrated by work at the South Tahoe plant [14] in which introduction of lime mud recycle from the chemical clarifier to the lime rapid mix reduced the mean effluent phosphate concentration from 0.22 to 0.16 mg P/ℓ. Recycling of scrubber water from the sludge and recalcining furnaces (which contained a total phosphate concentration of 12.8 mg P/ℓ, of which 12.3 mg P/ℓ was particulate) caused a reduction of the effluent orthophosphate from 0.16 to

0.09 mg P/ℓ. When these recycle streams were removed from the rapid lime mix basin and again introduced to the primary clarifier, the average effluent phosphate concentration increased from 0.09 to 0.31 mg P/ℓ.

Schmidt and McKinney [19] conducted laboratory tests of a chemical-biological scheme that is essentially similar to the PEP process except that it includes no provision for precipitate recycle. These workers used a lime dose of about 150 mg/ℓ $Ca(OH)_2$ to reach a pH of 9.5 in raw sewage precipitation. At this pH these authors claim that polyphosphates present in the raw sewage prevent the precipitation of calcium carbonate by adsorbing onto calcium carbonate nuclei. Since the major consumption of lime in a precipitation process is devoted to calcium carbonate precipitation, a reduction in lime dose will be obtained by this phenomenon. No full-scale or pilot-plant application of this work has been reported.

There are several activated sludge treatment plants in the United States at which phosphate removals are achieved that are far in excess of those predictable by normal biological means. There are two general schools of thought concerning the mechanism of these removals – that which proposes a biological mechanism ("luxury uptake") and that which proposes a chemical precipitation mechanism. Recent studies by Ferguson et al. [20] have demonstrated that the high removals of phosphate experienced at the Rilling Road Treatment Plant of San Antonio, Texas can be explained on the basis of a combination of calcium phosphate precipitation and reactor configuration (aeration basin design). This demonstration was based on the previous work of Menar and Jenkins [2] who explained the so-called luxury uptake of phosphate in terms of calcium phosphate precipitation. They proposed that precipitation occurred in an activated sludge aeration basin at a point where CO_2 stripping caused the pH to increase to the point that calcium phosphate precipitated. The behavior observed at San Antonio [21] could not be reproduced by a pilot plant operated by Menar and Jenkins [2] at San Ramon, California. Thus, at San Antonio soluble phosphate residuals of 1 to 2 mg P/ℓ were obtained at pH 7.8 to 7.9 while at San Ramon, even at pH values above 8.5, soluble phosphate concentrations of greater than 10 mg P/ℓ remained. Ferguson and McCarty [22] explained this difference in behavior based on the effects of carbonate and magnesium on phosphate precipitation proposing that in the lower alkalinity and magnesium concentrations at San Antonio (compared to San Ramon) more rapid calcium phosphate precipitation to form a more insoluble solid occurred. Ferguson et al. [20] proposed that apatite formation occurred significantly only during residence times typical of activated sludge treatment in the plug flow aeration basin of the Rilling Road activated sludge plant at San Antonio and not in the more back-mixed basins of the East and West plants.

Calcium phosphate precipitates formed in primary, secondary, or tertiary treatment units will tend to redissolve at the lower pH values encountered in anaerobic digestion. Indeed, redissolution of calcium phosphates precipitated in activated sludge aeration basins is found even in the slightly lower pH (higher CO_2) environment encountered in the sludge

blanket of a secondary clarifier [2]. Release of phosphorus has been generally observed from all activated sludges claimed to be showing "luxury uptake" when the sludges were exposed to anaerobic conditions and lowering of the pH.

SECTION V

MECHANISM OF CALCIUM PHOSPHATE PRECIPITATION

INTRODUCTION

Although the use of lime for precipitating calcium phosphate from wastewater has been suggested and tested widely, the mechanism of calcium phosphate precipitation from this medium is not well defined. For the conditions commonly encountered in wastewater, hydroxyapatite ($Ca_5OH(PO_4)_3$) is the thermodynamically stable solid calcium phosphate phase. The concentrations of dissolved calcium and phosphate in lime-treated domestic wastewaters, however, far exceed the equilibrium values of crystalline hydroxyapatite. It is therefore apparent that either precipitation kinetics or the presence of more soluble calcium phosphate phases control phosphate residuals in wastewaters treated with lime.

PRECIPITATION OF CALCIUM PHOSPHATE FROM CALCIUM PHOSPHATE SOLUTIONS

A considerable body of experimental work in chemically-defined solutions has shown that the initial solid phase that appears in the rapid precipitation of calcium orthophosphate from basic solutions is structurally noncrystalline. The noncrystalline structure is metastable and, if allowed to remain in contact with the preparative solution, it will spontaneously convert into a crystalline product with a chemical stoichiometry and X-ray diffraction pattern typical of the mineral apatite.

Recent kinetic studies by Stumm and Leckie [18] have defined three phases in calcium phosphate precipitation. These were: nucleation – the formation of amorphous calcium phosphate from solution; phase transformation – the slow transformation of amorphous calcium phosphate into crystalline apatite; and crystal growth of crystalline apatite. Phosphate is removed from solution during nucleation and crystal growth but not during phase transformation. Since the dissolved phosphate residual in equilibrium with crystalline apatite will be lower than that coexistent with the amorphous nucleating phase, Stumm and Leckie [18] suggested that low wastewater phosphate residuals might be obtained by recycle of preformed crystalline apatite to a precipitation reactor. Their suggestion was based on the observation that the presence of apatite crystals largely eliminated the phase transformation step between nucleation and crystal growth. Ferguson et al. [4] recently have demonstrated that the addition of such preformed precipitate to calcium phosphate carbonate

solutions supersaturated with respect to calcium phosphate, eliminates lag periods prior to precipitation that were observed in batch reactors not containing added precipitate.

There have been various reports of the nature of the calcium phosphate phase that precedes crystalline apatite. Strates et al. [23] suggest that dicalcium phosphate dihydrate ($CaHPO_4 \cdot 2H_2O$) first crystallizes and rapidly converts into apatite. McGregor and Brown [24] maintain that octacalcium phosphate $Ca_4H(PO_4)_3$ is the metastable precursor of apatite. Booth and Coates [25] suggest that dicalcium phosphate dihydrate is the first crystalline product to appear and it transforms into octacalcium phosphate, $Ca_4H(PO_4)_3$, which itself then transforms into apatite. Walton et al. [26] found that over the pH range 6.3 to 9.04 calcium phosphate (presumably apatite) was preceded by a metastable precursor of the stoichiometry but not the structure of tricalcium phosphate, $Ca_3(PO_4)_2$.

The stable crystalline apatite phase formed from pure calcium phosphate solutions, while yielding X-ray diffraction patterns typical of apatite ($Ca_5(PO_4)_3OH$), may deviate significantly in stoichiometry from the Ca/P mole ratio of 1.67 predicted from this formula. Such calcium deficient and other nonstoichiometric apatites have been reported over the entire range of Ca/P mole ratios from 1.33 to 2 [27] with crystal structures indistinguishable by X-ray diffraction from well-crystallized apatite.

Several theories have been advanced to explain the existence of these nonstoichiometric apatites – thus some workers [28] explain low Ca/P ratios by postulating the presence of adsorbed phosphate on the solid surface, possibly in the form of surface complexes. Rootare et al. [29] believe that these surface complexes control the phosphate concentration in a solution in equilibrium with apatite and are formed by hydrolysis of the apatite surface thus:

$$Ca_{10}(PO_4)_6(OH)_2 + 6H_2O \rightleftharpoons 2Ca^{2+} + 2HPO_4^{2-} + 4[Ca_2HPO_4(OH)_2] \qquad (1)$$

$$Ca_2HPO_4(OH)_2 \rightleftharpoons 2Ca^{2+} + HPO_4^{2-} + 2OH^- \qquad (2)$$

The evidence for the existence of such a complex is indirect – and largely based on a change in Ca/P mole ratio in solution from 1 to 1.67 as the concentration of an apatite suspension is decreased.

McConnell [30] suggests the simultaneous precipitation of lower Ca/P ratio solids together with apatite, e.g., brushite ($CaHPO_4$, Ca/P = 1) and octacalcium phosphate ($Ca_4H(PO_4)_3$, Ca/P = 1.33). However, this suggestion would not be valid if the apatite formed had no detectable phase impurities. Other investigators suggest the formation of apatite with a calcium deficient, defective lattice [31] as well as the isomorphous substitution of ions or groups for those normally present in the apatite lattice.

PRECIPITATION OF CALCIUM PHOSPHATE FROM SOLUTIONS CONTAINING MAGNESIUM AND CARBONATE

Domestic wastewaters contain a wide variety of organic and inorganic compounds, many of which might influence the precipitation of calcium phosphate. However, hydrogen ion (pH), magnesium, carbonate, and, to a lesser extent, fluoride (because of its low concentration in wastewaters), appear to be the most significant. Their effects will be reviewed in the context of the three steps of precipitation (nucleation, phase transformation, and crystal growth) defined by Stumm and Leckie [18].

Since pH influences the relative abundance of the various phosphate species and components of the carbonate system, it is important in determining the range of stability of various calcium phosphate solids. However, for pH values above 7 with solution Ca/P ratios of >0.5 the precipitation of monocalcium phosphate ($Ca(H_2PO_4)_2$) and its monohydrate ($Ca(H_2PO_4)_2 \cdot H_2O$) or dicalcium phosphate (monetite, $CaHPO_4$) and its hydrate (brushite, $CaHPO_4 \cdot 2H_2O$) are not important. In fact for commonly encountered wastewater Ca/P ratios, hydroxyapatite is the stable phase at all commonly encountered process pH values.

pH influences the stability of formed precipitates in the sense that at high pH values rapid precipitation of unstable solids results, whereas at lower pH values slower precipitation of more stable solids may occur. Walton et al. [26] reports that hydroxyl ion is directly involved in the formation of the critical nucleus in calcium phosphate precipitation and that the rate of nucleation is a function of $[OH^-]^2$. Eanes et al. [32] report that a pH increase causes a reduction in the rate of crystallization from the amorphous phase. They report that conversion to apatite was completed in 2.75 hr at an initial pH of 8.0, while at a pH of 9.8 complete conversion took place in 6.5 hr. The apparent stabilizing effect of the higher pH upon the noncrystalline phase is probably due to the incorporation of impurities into the precipitate during the more rapid high pH nucleation phase.

Magnesium has been reported to influence both the rate of calcium phosphate precipitation and the nature of the precipitated solid. It is not likely, however, that magnesium phosphate or carbonate solids will form for the ranges of magnesium, carbonate, and phosphate concentrations typical of wastewaters. Magnesium inhibits the nucleation of calcium phosphate, possibly due to the competition between magnesium and calcium ions and to the formation of the strong magnesium phosphate complex $MgPO_4^-$[33]. The presence of magnesium at calcium phosphate crystal growth sites has been postulated to slow down the transformation of amorphous calcium phosphate phases into apatite [4]. Newesely [34] has reported that anhydrous tricalcium phosphate and Mooney and Aia [35] have reported that beta tricalcium phosphate (whitlockite) form instead of apatite in the presence of magnesium. Whitlockite is often found with magnesium as a minor component – with contents of about 6 to 8 atom percent. Other metals, e.g. manganese and ferrous iron, also

stabilize whitlockite. Ferguson [3] has proposed that the presence of Mg/Ca mole ratios of greater than 5 stabilize beta tricalcium phosphate in sludge digestor liquors and proposed that in wastewaters of differing Ca/Mg ratios either apatite or a stabilized beta tricalcium phosphate may control the dissolved phosphate concentration.

In systems containing carbonate and phosphate the effect of Mg on calcium phosphate and carbonate precipitation appears to be complex and pH dependent. Magnesium is reported to interfere with the precipitation of the calcium carbonate solids, calcite and aragonite, by inhibition of nucleation and lattice distortion. Calcites containing magnesium as a minor component exist. These magnesian calcium carbonates are more soluble than calcite and their solubility increases with their magnesium content over the range 0-20%, from pK_{sp} 8.4 to pK_{sp} 6.3 (Chave et al. [36]).

Recent work in laboratory batch systems at phosphate, carbonate, and magnesium concentrations typical of wastewaters [4] showed that besides forming calcium carbonate and phosphate solids, carbonate and phosphate interacted in the formation of these respective solids. Carbonate has been reported by Ferguson et al. [4] to inhibit both the nucleation and phase transformation of calcium phosphates. Newesely [34] reported that carbonate at 0.8 mM disturbed the cyrstallization of calcium phosphate, and Ferguson [3] reported that no crystalline calcium phosphate is formed from solutions of typical wastewater constituent concentrations containing 10 mM carbonate. However, the presence of carbonates in bone, dentine, and enamel (all of which are apatite) and the existence of minerals such as francolite and collophane suggest the possibility of forming mixed calcium carbonate–phosphate compounds [28]. Rapid precipitation, as encountered in wastewater calcium phosphate precipitation processes, results in mixed calcium phosphate–carbonate solids because the discrimination between these radicals becomes difficult and recrystallization is a slow process. Simpson [37] has reported that high partial pressures of CO_2 destabilize apatite and has observed the formation of octacalcium phosphate at CO_2 partial pressures of between 0.01 and 0.1 atm. and at pH values below 8.1.

SURFACE PROPERTIES OF CALCIUM PHOSPHATE SUSPENSIONS

It is generally observed that calcium phosphate–carbonate suspensions settle well when produced at pH values greater than about 10 but that the opposite is true for suspensions produced at lower pH values than this. The stability of colloidal calcium phosphate–carbonate suspensions can be attributed to electrostatic repulsive forces created by a surface charge that originates from ionization of various groups on the solid side of the solid-liquid interface by isomorphous substitution, or by ion adsorption. Somasundaran [38] has suggested surface hydrolysis as a possible mechanism of charge development on apatite:

$$PO_4^{3-} + H_2O \rightleftarrows HPO_4^{2-} + OH^- \quad (3)$$

$$HPO_4^{2-} + H_2O \rightleftarrows H_2PO_4^- + OH^- \quad (4)$$

$$H_2PO_4^- + H_2O \rightleftarrows H_3PO_4 + OH^- \quad (5)$$

$$Ca^{2+} + OH^- \rightleftarrows CaOH^+ \quad (6)$$

$$CaOH^+ + OH^- \rightleftarrows Ca(OH)_2 \quad (7)$$

At low pH values reactions (3), (4), and (5) will proceed in the forward direction and (6) and (7) will proceed in the reverse direction, while at high pH values the reverse is true. It is also evident from reactions (3) through (7) that the charge on the solid surface depends on pH of the solution. Somasundaran [38] found the pH at the zero point of charge (pH_{zpc}) for apatite to be 6. Stumm and Morgan [33] argue that the pH_{zpc} of salt-type minerals depends in a complicated way on the pH and also on the concentration of all potential-determining ions. The presence of precipitate impurities changes the pH_{zpc} because the zpc of solids should correspond to the pH of the charge balance (electroneutrality) of potential-determining ions [39].

Calcium phosphate precipitation in wastewater treatment normally involves raising the pH to 10.5 or higher. At these pH values $Mg(OH)_2$ also precipitates and its formation has been proposed as a factor in improving the settling properties of the calcium phosphate–carbonate suspension. It is possible that specific adsorption of $Mg(OH)_2$ on the negative suspension surface [33] takes place. It is also possible that bridging occurs between $Mg(OH)_2$ and the surface phosphate groups leading to a three-dimensional network [40].

SUMMARY

Precipitates are formed in solutions as a result of nucleation followed by crystal growth. In calcium phosphate precipitation, however, crystal growth does not usually follow the nucleation process immediately, but is preceded by a lengthy phase transformation step. During the later step, the nucleated amorphous calcium phosphate is transformed into a crystalline phase with no net phosphate removal from solution.

Hydrogen ion concentration exerts a significant effect on each of the three phases of calcium phosphate precipitation. An increase in pH speeds up nucleation, while at the same time appears to cause a reduction

in the rate of crystallization. In addition, pH exerts a significant effect on the surface properties of the suspension.

Magnesium appears to inhibit the nucleation of calcium phosphate, to slow down the formation of apatite from amorphous calcium phosphate, and to stabilize the formation of tricalcium phosphate. It also tends to interfere with the precipitation of calcium carbonate. At pH values above 10.5, $Mg(OH)_2$ precipitates and appears to be involved in producing a readily flocculable calcium carbonate–phosphate suspension.

Carbonate appears to inhibit both the nucleation and the phase transformation of calcium phosphate. A high partial pressure of CO_2 reportedly destabilizes apatite and enhances the formation of octacalcium phosphate.

SECTION VI

APPROACH RATIONALE

The approach to the problem of predicting the dissolved phosphate residuals obtainable by calcium phosphate precipitation from wastewater was first to study a model or chemically-defined system representative of the relevant components of wastewater. The results of this study were then applied to the prediction of dissolved phosphate residuals obtained experimentally from wastewater.

The complex and variable nature of domestic wastewater makes the use of simple models difficult though necessary. This work used the model system, Ca - Mg - P_T - C_T - H^+ - H_2O, where $C_T = H_2CO_3 + HCO_3^- + CO_3^{2-}$ and $P_T = H_3PO_4 + H_2PO_4^- + HPO_4^{2-} + PO_4^{3-}$ with which previous authors [3,4, 22] have had some success in modelling waste treatment situations for calcium phosphate precipitation equilibria and kinetics. It must be realized, however, that since domestic sewage contains species such as polyphosphate, fluoride, and organic acids, as well as clay minerals and organic particulate solids, the use of a simplified system excluding these cannot provide an exact representation of the actual situation.

The components of the model system vary in domestic sewage over the approximate ranges indicated in Table 1. The pH in domestic wastewater is typically within the range 6.5 to 8, averaging about 7.5, but wastewaters subject to calcium phosphate precipitation may have pH values of up to 11.5. In the model chemically-defined system, the range of chemical conditions studied were purposely made wider than those cited in Table 1.

TABLE 1

COMPONENT CONCENTRATIONS IN WASTEWATER
(from Ferguson [3])

Component	Range mM	Typical Value mM
Calcium	0.5 – 5	1.5
Magnesium	0.25 – 1	0.5
Carbonate	2 – 8	4.0
Phosphate	0.1 – 0.5	0.3

The precipitation model described by Stumm and Leckie [18] was adopted as the basis for study of calcium phosphate precipitation. It was postulated, on the basis of the literature on calcium phosphate precipitation and a knowledge of the reaction times used in wastewater calcium phosphate precipitation processes, that a steady state amorphous calcium phosphate phase controlled the residual dissolved phosphate concentration. The validity of this steady state postulate was first tested and then the nature of the steady state phase was investigated.

The activity product variation of various phases with pH and solution composition was tested. The stoichiometry of the steady state phase was determined. Attempts were made to obtain crystallographic information from X-ray powder diffraction patterns of the aged precipitate.

The results obtained from the chemically-defined systems were applied to the precipitation of calcium phosphate by lime from wastewaters. Since it became evident, as the work progressed, that precipitate separation was a major factor in determining the total phosphate residual obtainable, the study devoted some attention to the chemical factors that influence the removal of precipitate by sedimentation.

Limited attention was also directed toward the effect of precipitate recycle on dissolved phosphate residual. This was prompted by the precipitation model and results of previous investigators who attributed low dissolved phosphate residuals to the growth of crystalline calcium phosphates.

SECTION VII

EXPERIMENTAL EQUIPMENT AND PROCEDURES

EXPERIMENTAL EQUIPMENT

The experimental phases of the study involved runs both in chemically-defined systems containing reagent grade chemicals dissolved in distilled water and in domestic wastewater from the SERL pilot plant. For the chemically-defined systems both continuous flow and batch reactors were employed. The experiments with sewage used a continuous flow system only.

Chemically-Defined Systems – Continuous Flow Experiments

Continuous flow experiments on chemically-defined systems were conducted in a single acrylic plastic CSTR with inside dimensions of 10 in. x 10 in. x 10 in. The reactor contents were mixed at 71 rpm by a stainless steel stake and stator stirrer mounted vertically and driven by a 1/8 hp DC motor (Bodine Co.) controlled by a Speed Controller (Minarik Co.). Power input was measured by a torquemeter that could be attached to the vertical stirrer shaft. Power input was such that an average velocity gradient of approximately 75 sec^{-1} was maintained in the experiments. To prevent precipitation in the feed lines and feed storage vessels prior to the reactor, it was necessary to prepare the chemical solutions in three separate batches and then mix these in a well-defined fashion just preceding their entry into the reactor. The bulk of the feed, which was either stored in 55-gal stainless steel drums or in a 1000-gal redwood tank lined with a plastic sheet contained the calcium, magnesium, and orthophosphate components. This solution was prepared by adding stock solutions of reagent grade $CaCl_2$, $MgCl_2$, and H_3PO_4 to distilled water (Figure 2).

After 30 min aeration to mix the solution and to produce a uniform pH of 3.5, the solution was pumped to a constant head tank using a stainless steel centrifugal pump. The solution then flowed by gravity through a 1/2-in. PVC pipe and a Brooks Full View Rotameter into the reactor. A concentrated NaOH solution (for pH adjustment) was pumped into the influent stream through a "T-joint" 20 in. ahead of the reactor inlet. At a point 2 in. before the reactor inlet the carbonate component (C_T) was added as a concentrated solution of sodium carbonate.

The reactor pH was monitored continuously using a Radiometer Model 22 pH meter and a combined calomel-glass electrode. The reactor effluent

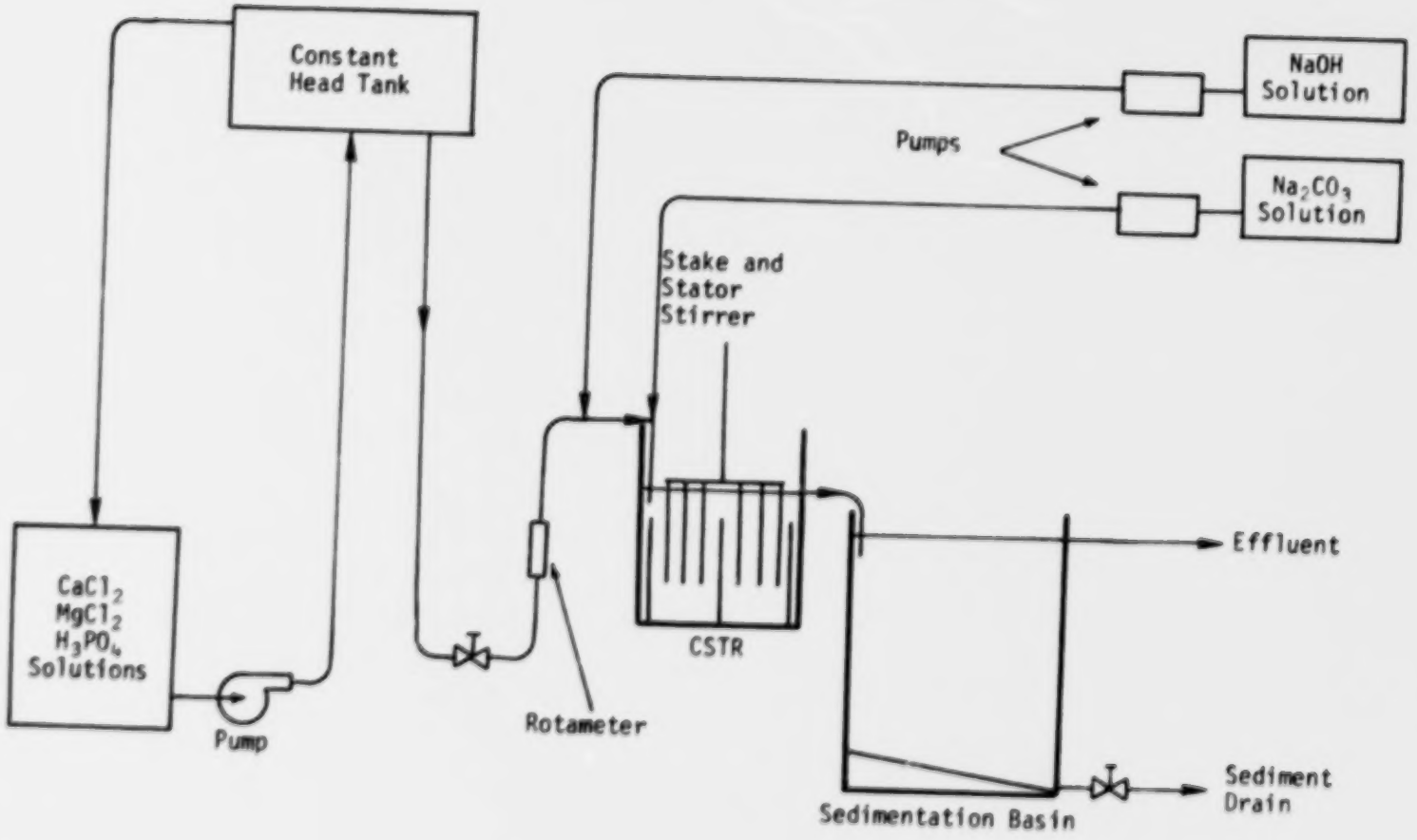


FIGURE 2. SCHEMATIC FLOWSHEET FOR EXPERIMENTS ON CHEMICALLY-DEFINED SYSTEMS

discharged through 1 1/2-in. PVC pipe. Samples for analysis of dissolved P_T, C_T, Ca, and Mg were taken from the reactor effluent pipe after steady state had been reached and filtered immediately through 0.45-μ membrane filters (Millipore HA). When it was desired to collect precipitate samples for X-ray diffraction analysis, the reactor effluent was collected in a 30-ℓ sedimentation basin.

In continuouous flow experiments employing a recycle of suspension, a circular 12-ℓ concave-bottomed sedimentation basin followed the completely mixed reactor in the flow-scheme illustrated in Figure 3. Suspension was recycled to the reactor from the underflow of the sedimentation basin using a peristaltic pump (Sigmamotor Model T65). In these experiments the mean hydraulic residence times were 42 min in the reactor and 34 min in the sedimentation basin. Sufficient feed solution for several days of continuous operation was prepared by adding reagent grade $CaCl_2$, $MgCl_2$, and H_3PO_4 to 3000 ℓ of well-mixed tap water held in a 1000-gal polyethylene-lined redwood tank. The performance of the recycle reactor was monitored on the basis of grab samples taken from the sedimentation basin overflow.

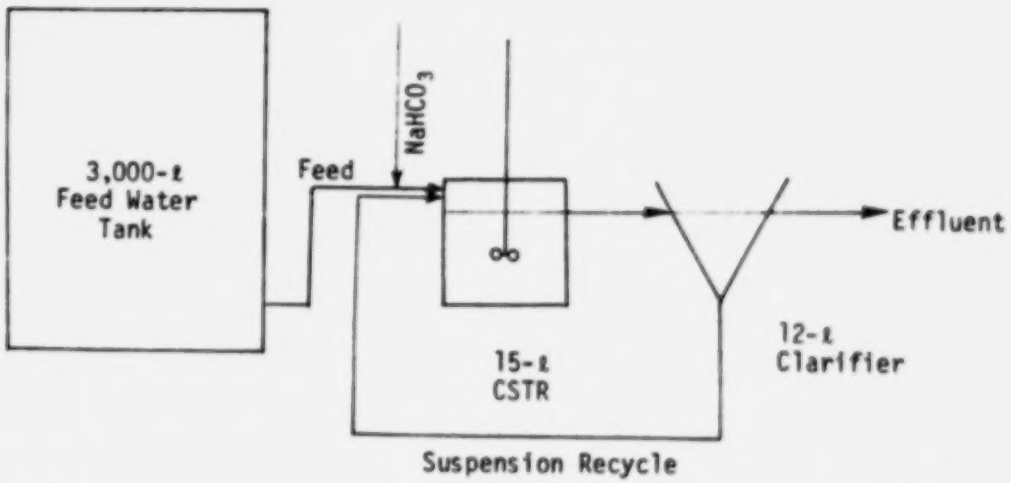


FIGURE 3. SCHEMATIC OF CALCIUM PHOSPHATE PRECIPITATION WITH SUSPENSION RECYCLE

Chemically-Defined Systems — Batch Experiments

Batch experiments were conducted on chemically-defined systems when it was demonstrated that they could be expected to yield information that was identical to that obtained in continuous flow, steady state system. In these batch experiments the reactor was a magnetically stirred 4-ℓ beaker. Predetermined amounts of Na_2CO_3 and H_3PO_4 stock solutions were mixed rapidly into 4 ℓ of distilled water in a batch reactor and the pH

of the mixture adjusted immediately to the desired value with NaOH solution. A mixture of the desired amounts of $CaCl_2$ and $MgCl_2$ stock solutions were then added rapidly to the stirred solution and at that time the measurement of reaction time was started. A 15-min reaction time was employed in these experiments on the basis of results from continuous flow studies. During this reaction time the pH was monitored and maintained constant by NaOH addition. Samples for the analysis of dissolved C_T, P_T, Mg, and Ca were withdrawn after 15 min and immediately filtered through 0.45-μ membrane filters.

Wastewater Experiments

Continuous flow wastewater precipitation experiments were conducted in a 3-compartment epoxy-coated galvanized steel reactor of which each compartment was 15 in. x 15 in. x 15.8 in. water depth. The contents of each compartment were stirred by straight blade turbine paddles mounted on a vertical shaft. The precipitation unit was an integral part of a chemical-biological process train that, in addition to lime addition, precipitation reactors, and two sedimentation basins, contained a recarbonation basin and clinoptilolite columns for ammonia removal (Figure 4).

Sufficient lime slurry for 24-hr operation was prepared by adding quicklime to 100 ℓ of tap water in a 30-gal plastic bin. The lime slurry was made up to a concentration of either 300 mM or 600 mM, depending on what pH of operation was desired. Lime slurry batches were analyzed for CaO immediately after preparation and immediately prior to the preparation of a fresh batch. Lime doses were computed on the basis of these analyses combined with measurement of the volume of lime slurry pumped. The lime slurry was introduced into the wastewater feed at a point 2 in. ahead of the first reactor and at a rate that was determined by a pH controller in the reactor, preset to the desired pH value.

After passing through the three reactor compartments, the wastewater entered a circular concave-bottom sedimentation basin. The performance of the precipitation unit was monitored by analysis of samples which were collected continuously from the effluent of the sedimentation basin. Samples of both influent and effluent were stored at 4°C between sampling and analysis. In addition to the analyses conducted on the chemically-defined systems, measurements of total orthophosphate and dissolved hydrolyzable phosphate plus orthophosphate were made on samples of influent, lime precipitated effluent, the recarbonated effluent, and the clinoptilolite column effluent. Each experimental run with the wastewater treatment plant lasted for at least four days.

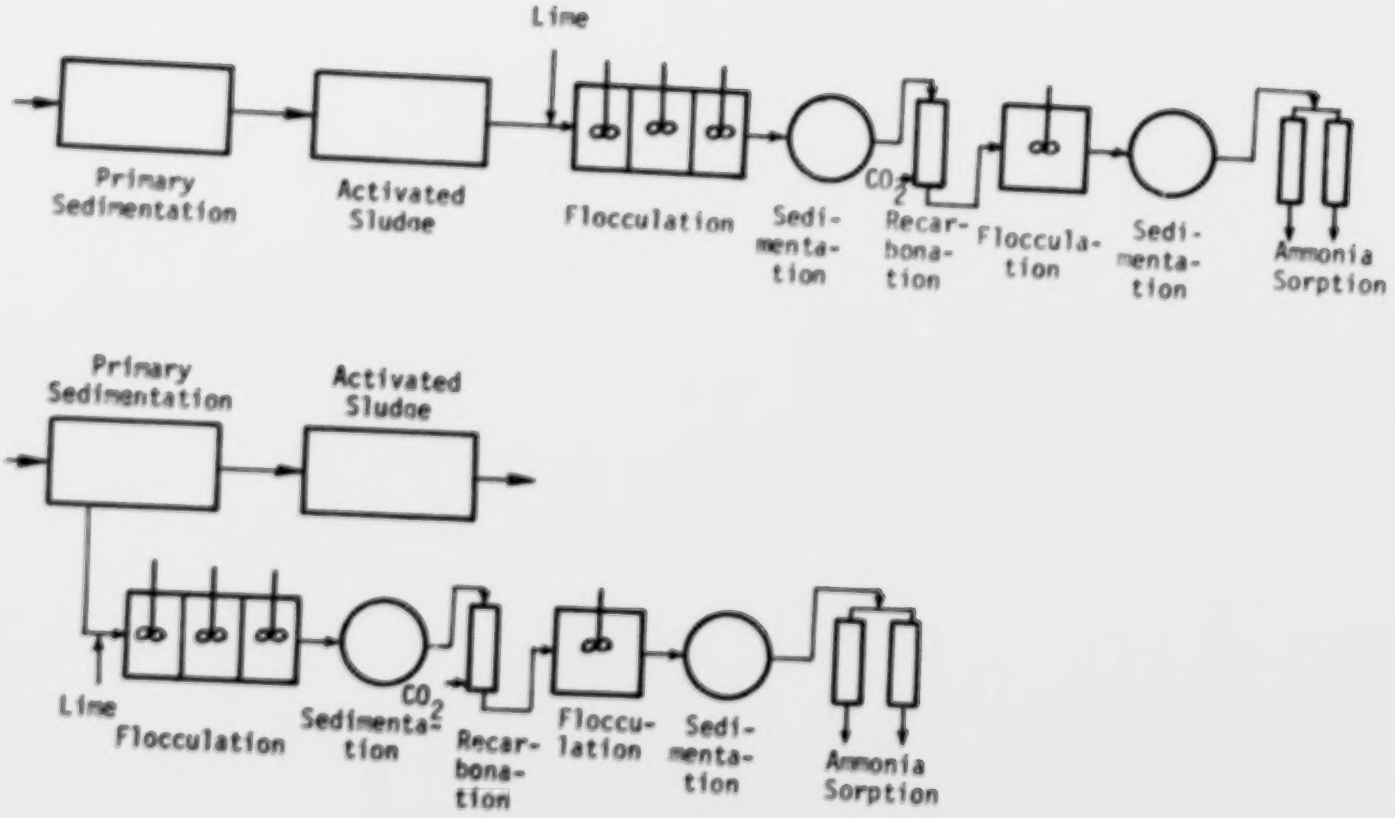


FIGURE 4. TREATMENT SYSTEMS USED IN STUDIES AT SERL PILOT PLANT

ANALYTICAL PROCEDURES

Sampling Procedures

Sampling procedures varied with the system under investigation and have been discussed previously with descriptions of the experimental systems.

Analytical Methods

Chemical and physical analyses were generally performed in accordance with *Standard Methods* [41], the *FWPCA Methods for Chemical Analysis* [42], or the *SERL Analytical Methods* [43]. The following brief description of analytical methods is presented to indicate method selection and any novel method modification employed.

Soluble Calcium. Soluble calcium was determined by EDTA titration using hydroxynaphthol blue indicator [43].

Total Hardness. Total hardness was determined by EDTA titration using calmagite indicator [43].

Magnesium. Magnesium was determined by the difference between the total hardness and the calcium concentrations.

pH. pH measurements were made using a Radiometer 22 pH Meter.

Total Phosphate. Total phosphate was determined on a sample after alkaline ashing. A suitable sample volume (usually 10 ml) was treated with 1 ml of 5% $MgCl_2 \cdot 6H_2O$ solution and evaporated to dryness on a steam table. The dried sample was ashed at 800°C for 1 hr. The residue was heated on a steam table for 30 min with 3 ml strong acid molybdate solution and after cooling was transferred to a 100-ml volumetric flask. Aminonaphthol-sulfonic acid (4 ml) was added and the volume made up to 100 ml. The absorbance of the molybdenum blue was read at 630 nm after 6 min using a 1-in. cell in a Bausch and Lomb Spectronic 20. The concentrations of all reagents were as presented in the 10th Edition of *Standard Methods* [41].

Dissolved Phosphate. Dissolved phosphate was determined by filtering the sample through 0.45-μ membrane filters and then proceeding as for the total phosphate.

Orthophosphate. Orthophosphate was determined using the aminonaphthol sulfonic acid (ANS) method outlined in the 10th Edition of *Standard Methods* [41] with the following modifications:

- Absorbance was read at 630 nm instead of 690 nm.
- Three ml of strong-acid molybdate was used instead of 4 ml.

. Six min reaction time was used instead of 10 min. The two latter modifications were made to reduce the possibility of polyphosphate hydrolysis during the orthophosphate analysis.

Ortho + Hydrolyzable Phosphate. A 50-ml sample was placed in a 125-ml Erlenmeyer flask and 1 ml of strong acid solution (310 ml conc. H_2SO_4 to 600 ml distilled water) was added. The sample was boiled gently for 30 to 40 min. Phenolphthalein (3 drops) was followed by 1 N NaOH until a pink color developed. This was discharged by the addition of strong acid solution. The sample was cooled and diluted to 50 ml and the analysis continued as for orthophosphate.

Inorganic Carbon. Inorganic carbon was determined with a Beckman Carbon Analyzer, Model 215A.

Alkalinity. Alkalinity was determined by titration with standard acid to a pH of 4.3.

Suspended Solids. Suspended solids were determined by the membrane filter technique of Winneberger et al. [44] using 0.45-μ membrane filters.

Suspension Settling Tests. Settling tests were conducted on reactor effluent by collecting it in a 4-ℓ beaker and allowing it to settle quiescently for 30 min. The settling properties of the suspension were evaluated in terms of the total phosphate removal achieved during this period by taking samples for total phosphate analysis before and after settling, using a pipette to sample 1 in. below the surface of the reactor effluent.

X-Ray Powder Diffraction Analysis. Suspensions for X-ray powder diffraction analysis were removed from the bottom of the sedimentation basin following the CSTP and centrifuged at about 1000 rpm. After decanting the supernatant, the suspension was quickly frozen by immersion in a dry ice-n-butyl alcohol mixture. The frozen suspension was lyophilized for a period of 48 hr. The X-ray powder diffraction pattern was determined using a Norelco diffractometer and scanning the spectrum from 4 degrees to 60 degrees. Because early experience demonstrated the presence of noncrystalline materials, lyophilization was later replaced by air-drying.

Lime Purity. A 0.5-gram finely pulverized sample was dissolved in 100 ml of a 10% sugar solution after one hour on a shaking machine. The solution was filtered and a 25-ml aliquot was titrated with 0.1 N sulfuric acid, using phenolphthalein indicator.

Total $Ca(OH)_2$. Total $Ca(OH)_2$ was determined on a sample of lime slurry after 30 min refluxing with HCl. A suitable sample volume (usually 10 ml) was added to 25.00 ml of 1 N HCl solution and the mixture was refluxed for 30 min. After cooling to room temperature the excess HCl was back-titrated with 1 N NaOH using phenolphthalein indicator.

SECTION VIII

PRECIPITATION OF CALCIUM PHOSPHATE IN CHEMICALLY-DEFINED SYSTEMS

INTRODUCTION

Batch and CSTR work in chemically-defined systems took the form of a series of experiments in which one or another of the components of the Ca - C_T - P_T - H^+ - Mg - H_2O system was varied singly to determine its effect on the residual phosphate or other component concentrations. The range over which individual component concentrations were varied was selected to cover the range commonly encountered in wastewater treatment. Nominal residence times of 15 min were generally used in CSTR experiments and a reaction time of 15 min was used in the batch experiments. Some kinetic studies employed variable detention (CSTR) and reaction (batch) times.

TIME TO ESTABLISH STEADY STATE

Prior to conducting experiments to determine the effect of various solution components on the phosphate residuals obtained by calcium phosphate precipitation, it was necessary to determine the time required to reach steady state values of phosphate residual that were representative of these precipitation processes. From the previous discussion of the phases involved in the precipitation of calcium phosphate from aqueous solution, it might be surmized that steady state dissolved phosphate residuals might be reached rather rapidly – at least within a few minutes of mixing reactants to produce a supersaturated solution. The period over which this steady state dissolved phosphate level is maintained is of importance since it is necessary to know whether measurements made soon after the initial attainment of steady state are representative of the conditions that might exist in phosphate precipitation reactors of longer residence times.

To establish the time required to reach steady state and the duration of this steady state condition, a series of batch and CSTR experiments were conducted under conditions typical of wastewaters. Three series of batch experiments at 23°C were conducted for systems containing Ca and P_T only, Ca, P_T, and C_T, and Ca, P_T, C_T, and Mg. The initial concentration of each of these components is summarized in Table 2. Each of these systems was examined at pH values of 8.0, 9.0, 10.0, and 11.0 – values that were maintained constant throughout the experiments by addition of NaOH

Preceding page blank

TABLE 2

INITIAL COMPOSITION OF BATCH SYSTEMS USED TO DEFINE TIME TO REACH STEADY STATE

Run	mM			
	Ca	P_T	C_T	Mg
I	2.0	0.5	-	-
II	2.0	0.5	2.0	-
III	2.0	0.5	2.0	2.0

Figure 5 shows that in each of the batch experiments steady state was reached in less than 10 min. Neither the introduction of carbonate (Run II) nor carbonate and magnesium (Run III) into the system lengthened the time required to reach steady state, although changes in the levels of steady state phosphate concentration were observed.

CSTR experiments at pH 8 were conducted with nominal reactor detention times varying from 3 to 200 min and with the initial concentrations of reactants reported in Figure 6. Because of their time-consuming nature and because of the results of the previous batch experiments, the CSTR runs were only conducted for a limited range of conditions. Thus only solutions containing Ca and P_T were tested in CSTR runs because batch experiments had indicated that the presence of Mg and C_T did not affect the time taken to attain steady state. Also since the batch experiments indicated a slightly slower rate of attainment of steady state at pH 8, the CSTR experiments were conducted at this pH value.

In all of the CSTR experiments, steady state dissolved phosphate concentrations were reached in less than a 10-min mean residence time and maintained for up to at least 200 min – a residence time typical of a phosphate precipitation process. On the basis of these results, reaction times of 15 min (batch or CSTR) were selected as being truly representative of the steady state conditions existing in nonrecycle wastewater calcium phosphate precipitation processes.

THE NATURE OF THE STEADY STATE SOLID PHASE

It is important to determine the solubility characteristics and the nature of the steady state solid phase that forms under conditions representative of wastewater calcium phosphate precipitation processes. An insight into the stoichiometry and solubility behavior of this solid was obtained by

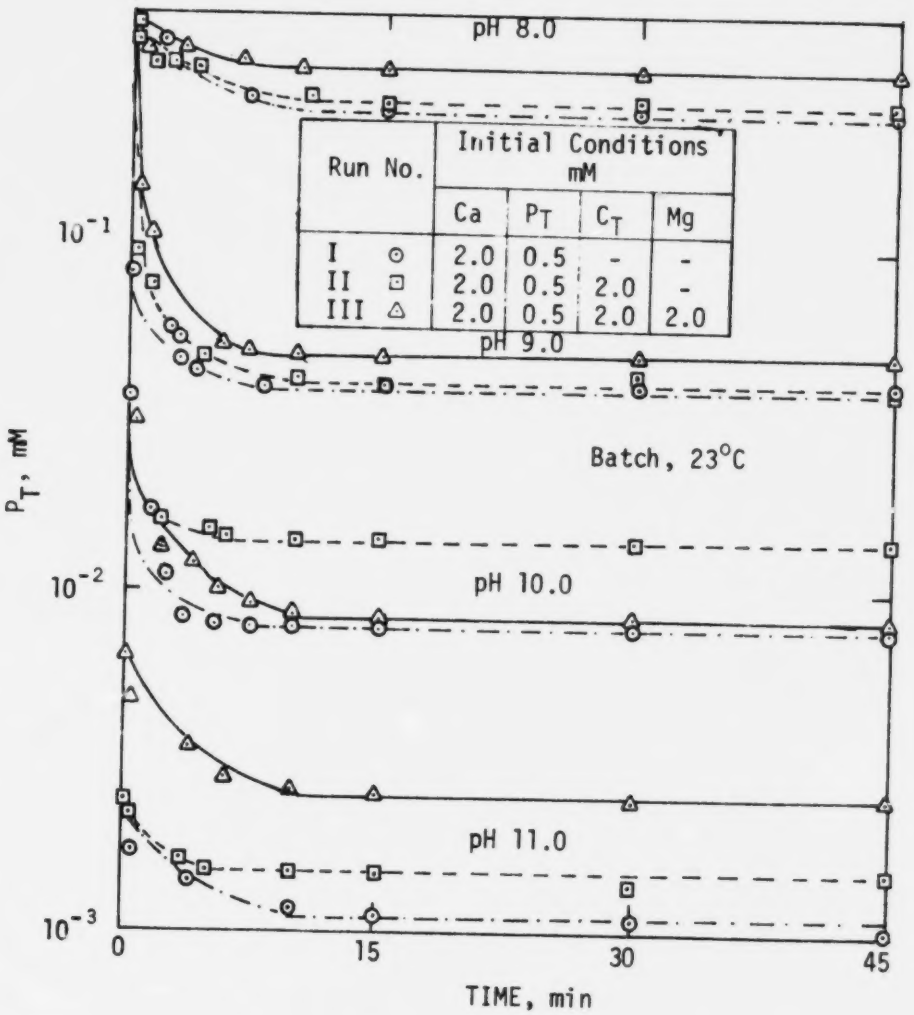


FIGURE 5. DEPENDENCE OF STEADY STATE P_T CONCENTRATION ON SOLUTION COMPOSITION AND pH IN BATCH REACTORS

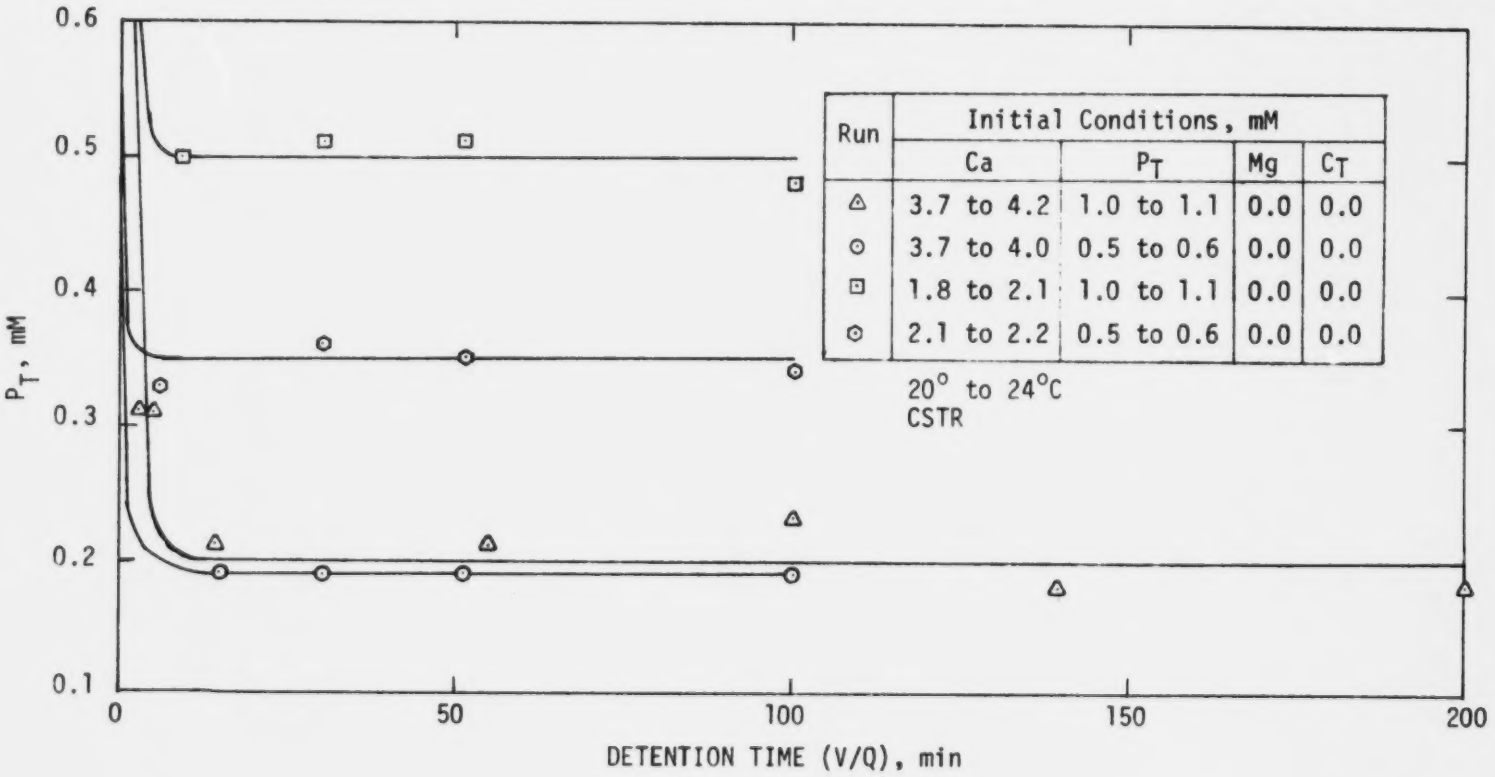


FIGURE 6. DEPENDENCE OF STEADY STATE P_T CONCENTRATION ON DETENTION TIME IN CSTR EXPERIMENTS

analysis of both steady state solid and liquid composition of batch and CSTR experiments.

CSTR experiments were conducted between 19° and 23°C with chemically-defined solutions in which initial component concentrations were in the ranges: Ca, 2.1 to 2.4 mM; Mg, 0 to 0.6 mM; P_T, 0.3 to 0.5 mM; C_T, 0 to 14.8 mM; pH 8 to 11. The initial mole ratios of the various components varied as follows: Ca/P, 3.9 to 6.7; Ca/Mg, 2.1 to 4.8; Ca/C_T, 0.2 to 2.4.

Batch experiments with 15 min reaction time were conducted at 19° to 23°C using initial solution concentrations in the range: Ca, 0.4 to 5.5 mM; Mg, 0.1 to 0.5 mM; P_T, 0.3 to 0.4 mM; C_T, 0.8 to 2.7 mM; pH 8 to 11. The initial mole ratios of the various components varied as follows: Ca/P_T, 1.1 to 17.2; Ca/Mg, 6.9 to 12.9; Ca/C_T, 2.0 to 7.3.

In all of these experiments nucleation proceeded without detectable lag period and steady state dissolved phosphate levels were reached within a 10-min period. The nature of the steady state solid can be circumstantially deduced, and a useful tool to predict steady state dissolved phosphate residual can be obtained by computing the activity product of various postulated solids from the steady state dissolved component data. This procedure was initially performed for selected experimental data for the several solids that have been postulated as apatite precursors and therefore might be expected to be present under steady state conditions prior to transformation to an equilibrium solid. Figure 7 is a plot of the negative logarithm of the activity product (pA) versus pH for the solids, dicalcium phosphate (DCP) ($CaHPO_4$), octacalcium phosphate (OCP) ($Ca_4H(PO_4)_3$), hydroxyapatite (HAP) ($Ca_5(OH)(PO_4)_3$) and tricalcium phosphate (TCP) ($Ca_3(PO_4)_2$). It is evident from Figure 7 that only the activity product for TCP appears to be constant over the entire pH range (8 to 11) of the experiments. Following this evidence further, Figure 8 presents a plot of pA of TCP for all data points (both batch and CSTR) collected in chemically-defined systems. The regression line fitted to these data points has the form:

$$pA = -0.064\ pH + 24.15 \qquad (8)$$

indicating the virtual constancy of the activity product with pH over the range pH 8 to 11.

This value of the negative logarithm of the activity product of TCP which averages 23.56 is somewhat lower than values reported in the literature which range from approximately 25 to 29 [45-47]. By using the plotting technique of Walton et al. [26] (Appendix A), which determines the stoichiometry of a nucleating solid phase, Figure 9 shows that the Ca/P mole ratio in the precipitate is 1.44. This value is very close to the stoichiometry of TCP which would give a theoretical Ca/P mole ratio of 1.5

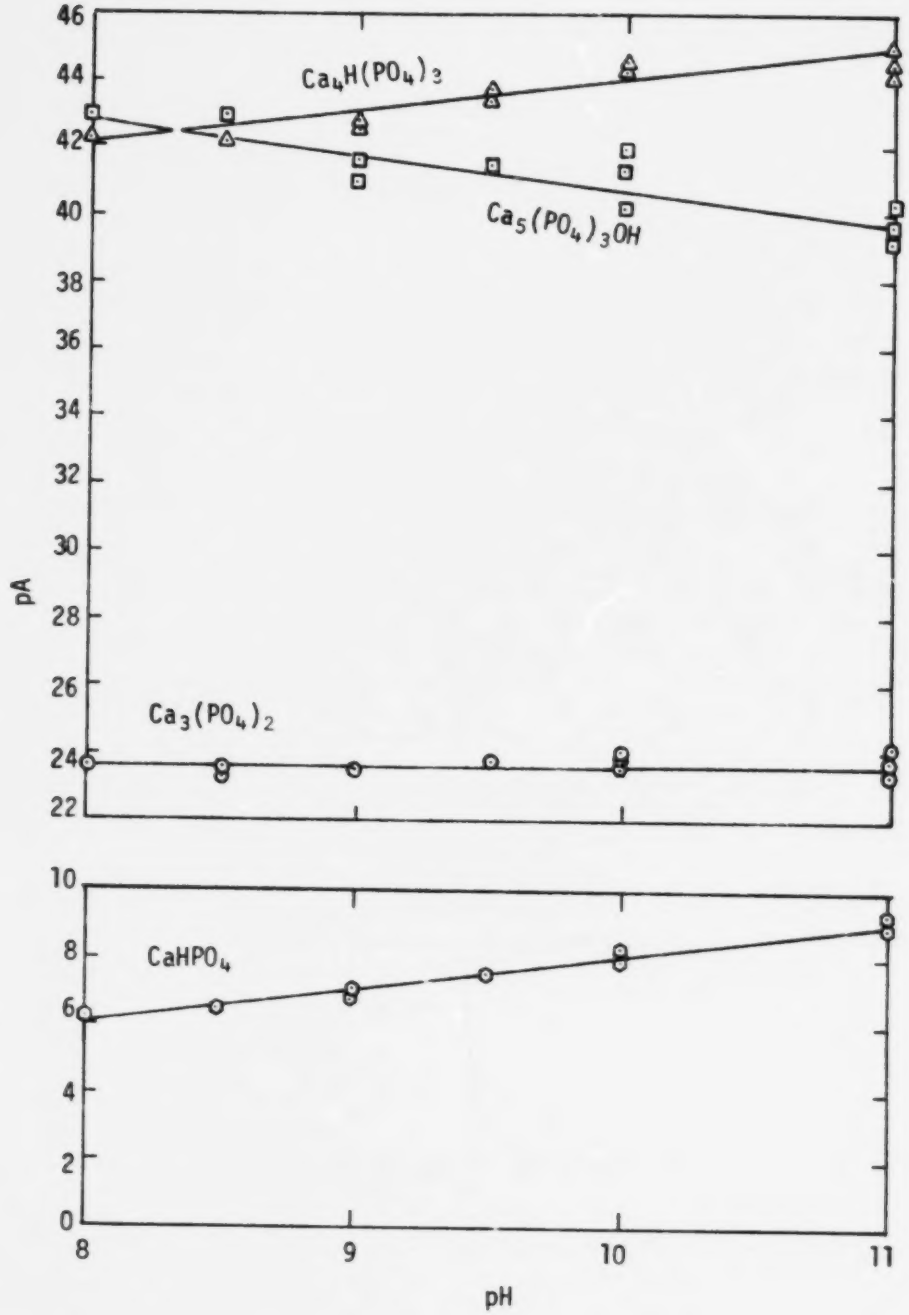


FIGURE 7. EFFECT OF pH ON pA FOR VARIOUS CALCIUM PHOSPHATE SOLIDS

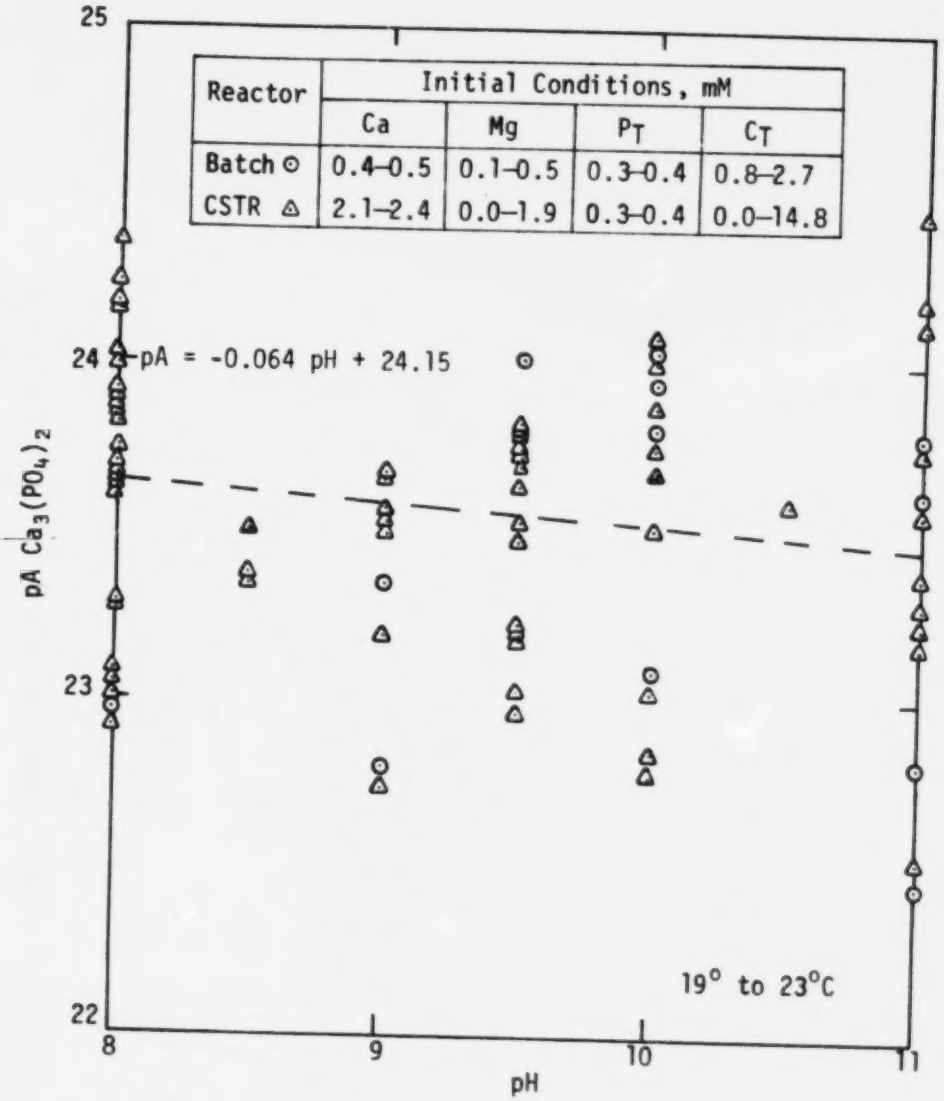


FIGURE 8. EFFECT OF pH ON pA OF TRICALCIUM PHOSPHATE

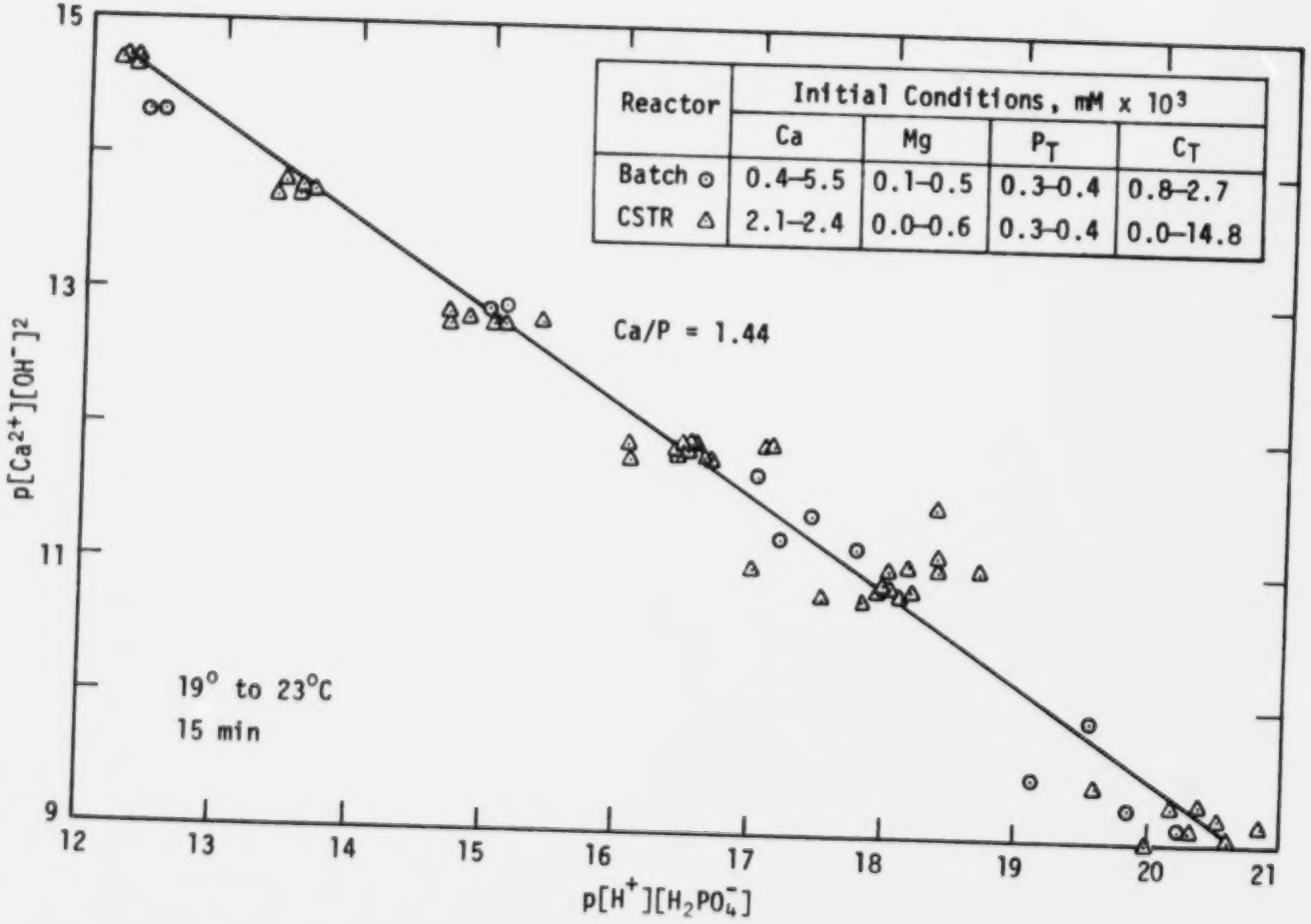


FIGURE 9. CRITICAL IONIC CONCENTRATIONS IN BATCH AND CSTR EXPERIMENTS

X-ray powder diffraction analysis of the solids produced in CSTR experiments failed to reveal the presence of any crystalline calcium phosphate. For experiments conducted at pH 10 and higher, crystalline calcite ($CaCO_3$) was detected. The X-ray analyses indicate that the steady state calcium phosphate solid is amorphous in nature – a fact that is supported by the lower pA values obtained here for TCP in comparison to those values reported in the literature.

EFFECT OF SOLUTION COMPOSITION ON STEADY STATE PHOSPHATE RESIDUAL

Even though the evidence produced in the previous section tends to support the presence of TCP as a steady state solid phase, there is a considerable range of variation in the values of the activity product of TCP at each of the pH values examined. While such variation (over about 1 to 2 orders of magnitude in pA) is common in equilibrium data derived from heterogeneous systems, it is necessary to determine whether these variations are in any way related to the concentrations of other important solution components – especially to the concentration of C_T and Mg. In the data analysis that follows, the effect of both of these components on the activity product of TCP and composition of the steady state solid phase is examined.

Effect of Magnesium

Previous reports have indicated that magnesium concentration is an important factor in calcium phosphate precipitation under conditions typical of wastewaters. Its effects have been classified as equilibrium effects (in which the solid calcium phosphate phase is altered by the presence of magnesium) and kinetic (in which the rate of attainment of equilibrium or steady state phosphate residuals is influenced by magnesium concentration). An additional "process effect" can be visualized, i.e., in which magnesium influences the separability of precipitated solids.

The influence of magnesium on steady state dissolved phosphate residual was tested in five series of CSTR experiments for which the initial component concentrations are listed in Table 3.

For the range of magnesium concentrations (more correctly Ca/Mg ratios) commonly encountered in wastewaters, the pA of TCP does not appear to be affected by magnesium concentration. Thus Figure 10 shows that only when initial Ca/Mg ratios were less than 0.6 (commonly most wastewaters have Ca/Mg ratios in the range of 1.5 to 6) did the activity product of TCP increase significantly. These results were supported by an additional series of CSTR experiments in which the steady state levels of dissolved P_T, C_T, Ca, and Mg were measured as a function of varying initial magnesium concentration in the range 0.5 to 10.9 mM. In this series of experiments the pH was maintained constant at 9.5, and the initial component concentrations were constant at Ca, 2.2 mM; P_T, 0.38 mM, and

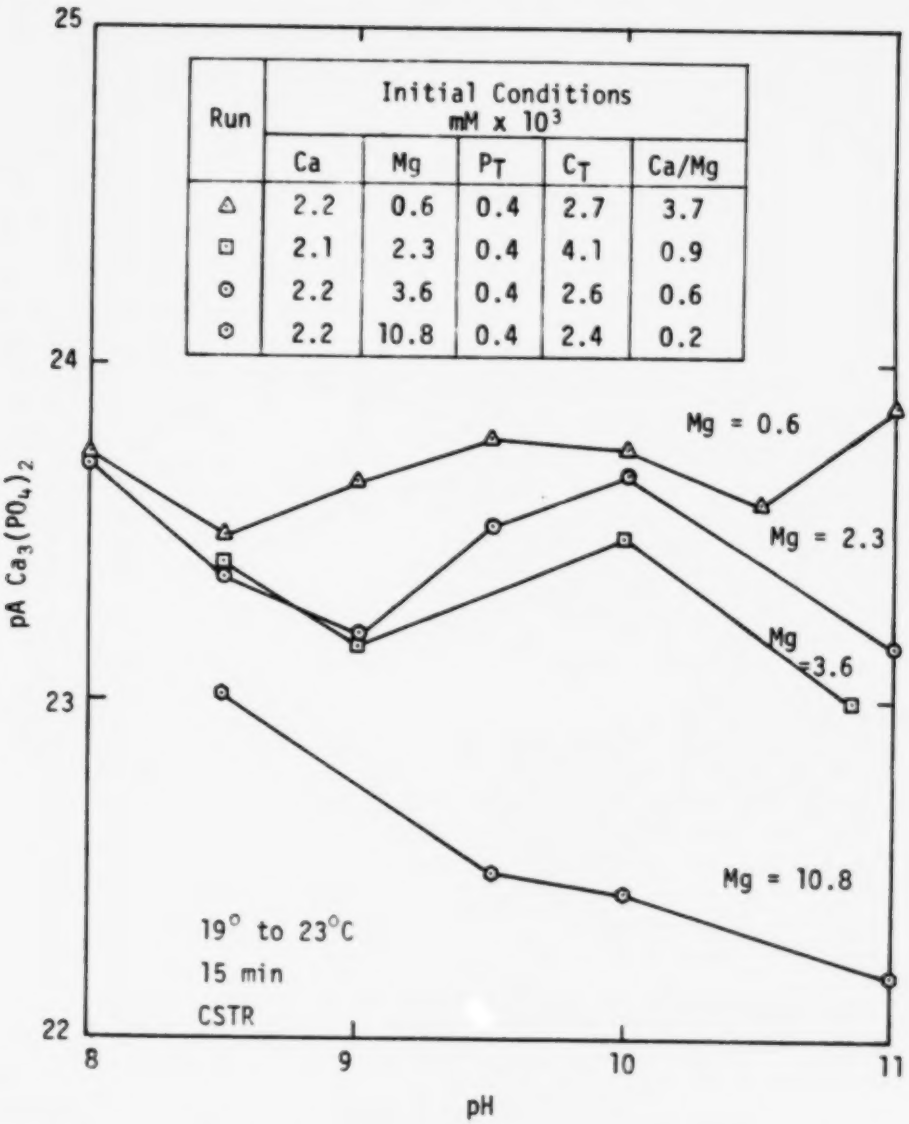


FIGURE 10. EFFECT OF Mg ON pA $Ca_3(PO_4)_2$

TABLE 3

INITIAL CONCENTRATIONS IN CSTR EXPERIMENTS
TO DETERMINE EFFECT OF MAGNESIUM

Experiment No.	mM				Mole Ratio		
	Ca	P_T	C_T	Mg	Ca/P_T	Ca/Mg	Ca/C_T
1	2.2	0.4	2.7	0.6	6.0	3.7	0.8
2	2.1	0.4	4.1	2.3	5.8	0.9	5.1
3	2.2	0.4	2.6	3.6	6.1	0.6	0.8
4	2.2	0.4	2.4	10.8	6.1	0.2	0.9

C_T, 2.5 mM. The data in Figure 11 indicate that no significant increase in residual dissolved phosphate occurred until the initial magnesium concentration was greater than 2 mM resulting in an initial Ca/Mg mole ratio of less than 1.

As in previous experiments, X-ray powder diffraction analyses failed to detect crystalline calcium phosphate in any of the solids derived from these CSTR experiments. Crystalline calcite ($CaCO_3$) was detected in suspensions produced from solutions containing initial calcium concentrations of 2.1 to 2.2 mM and initial magnesium concentrations of 0.5 mM. Suspensions produced from solutions in which the initial calcium concentration was 2.1 mM and the initial magnesium concentration was 2.3 mM failed to show the presence of crystalline calcite even after 1000 hr of contact between the suspension and the solution from which it was produced. After 4000 hr of solution-suspension contact a crystalline calcium carbonate, designated as Calcite III, was detected in the suspension.

Effect of Carbonate

The effect of carbonate on the precipitation of calcium phosphate from wastewaters has been interpreted both in terms of a competition between the calcium phosphate and calcium carbonate solids for calcium ion and by the modification of calcium phosphate solids such as apatites by the incorporation of carbonate. Both of these interpretations predict that the effect of increasing carbonate concentration will generally be to increase dissolved phosphate residual at a given calcium dose or conversely to require a higher calcium dose to reach the same phosphate residual.

Experiments on chemically-defined solutions were undertaken in CSTR systems with 15 min nominal residence time to determine the significance of the effect of carbonate on dissolved phosphate residuals at concentrations and under conditions that typified wastewater calcium phosphate

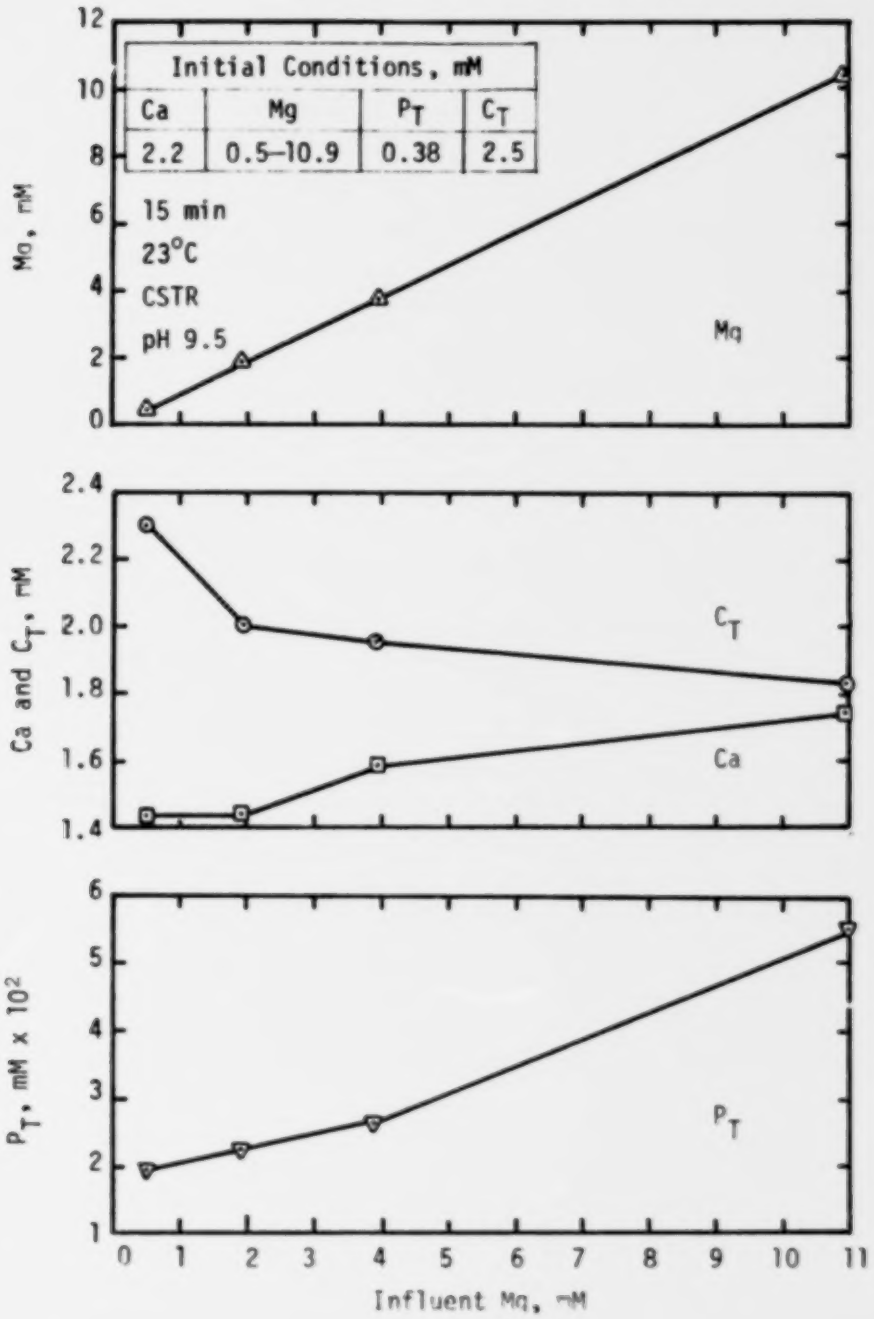


FIGURE 11. INFLUENCE OF Mg ON STEADY STATE CONCENTRATIONS OF Ca, Mg, C_T, AND P_T AT pH 9.5

precipitation processes. Initially four series of CSTR experiments were conducted with the initial conditions as outlined in Table 4. The results of these experiments, presented in Figure 12, show that up to initial C_T concentrations of 10.6 mM no significant effect on the activity product of TCP was detectable. At initial C_T levels of between 10.6 and 14.8 mM the activity product of TCP increased significantly for pH values above 9.5.

TABLE 4

INITIAL CONDITIONS FOR CSTR EXPERIMENTS TO DETERMINE EFFECT OF CARBONATE (C_T)

Exp. No.	pH Range	mM				Mole Ratio		
		Ca	Mg	P_T	C_T	Ca/Mg	Ca/C_T	Ca/P_T
1	8 –11	2.1–2.4	0–0.5	0.3–0.5	0	4.8–6.0	-	3.9–6.5
2	8 –11	2.2	0.6	0.4	2.5–2.7	3.7	0.8–0.9	6
3	8 –11	2.1–2.3	0–0.6	0.4–0.5	5.0–7.2	3.8–5.2	0.4	4.2–6.2
4	8.5–11	2.1–2.3	0.6	0.4	10.6–14.8	3.5–3.9	0.2	3.9–6.5

The effect this increase in activity product had on phosphate residual at pH 9.5 and 11 in systems containing calcium, magnesium, phosphate, and carbonate is illustrated in Figures 13 and 14 which are the results of 15-min nominal residence time CSTR experiments conducted at the range of initial experimental conditions depicted in Table 5.

TABLE 5

INITIAL CONDITIONS FOR CSTR EXPERIMENTS TO DETERMINE EFFECT OF CARBONATE ON PHOSPHATE AND OTHER COMPONENT RESIDUALS

pH	mM				Mole Ratio		
	Ca	Mg	P_T	C_T	Ca/Mg	Ca/C_T	Ca/P_T
9.5	2.0–2.2	0.6	0.4	2.6–14.4	3.4–3.7	0.1–0.9	4.4–6.1
11.0	2.2–2.3	0.6	0.4	2.5–14.8	3.7–3.8	0.1–0.9	6.0–6.1

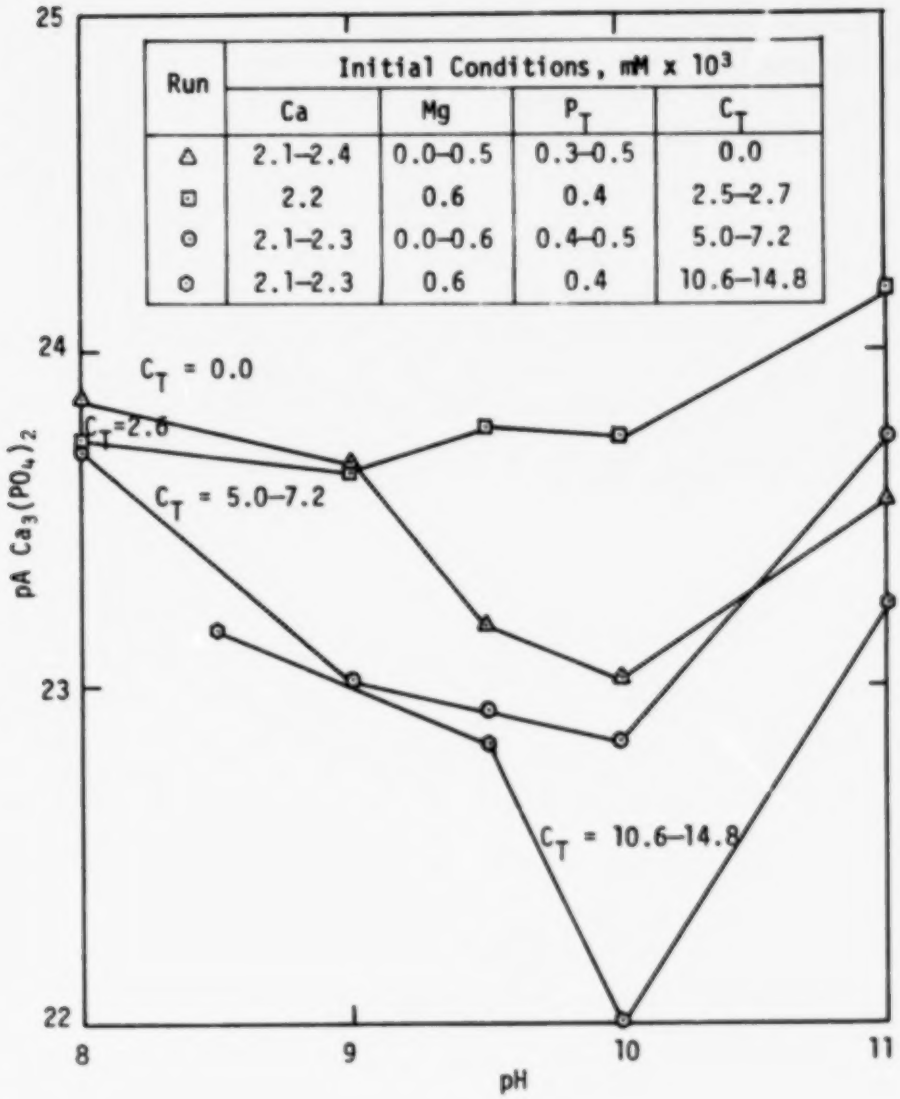


FIGURE 12. EFFECT OF C_T ON pA $Ca_3(PO_4)_2$

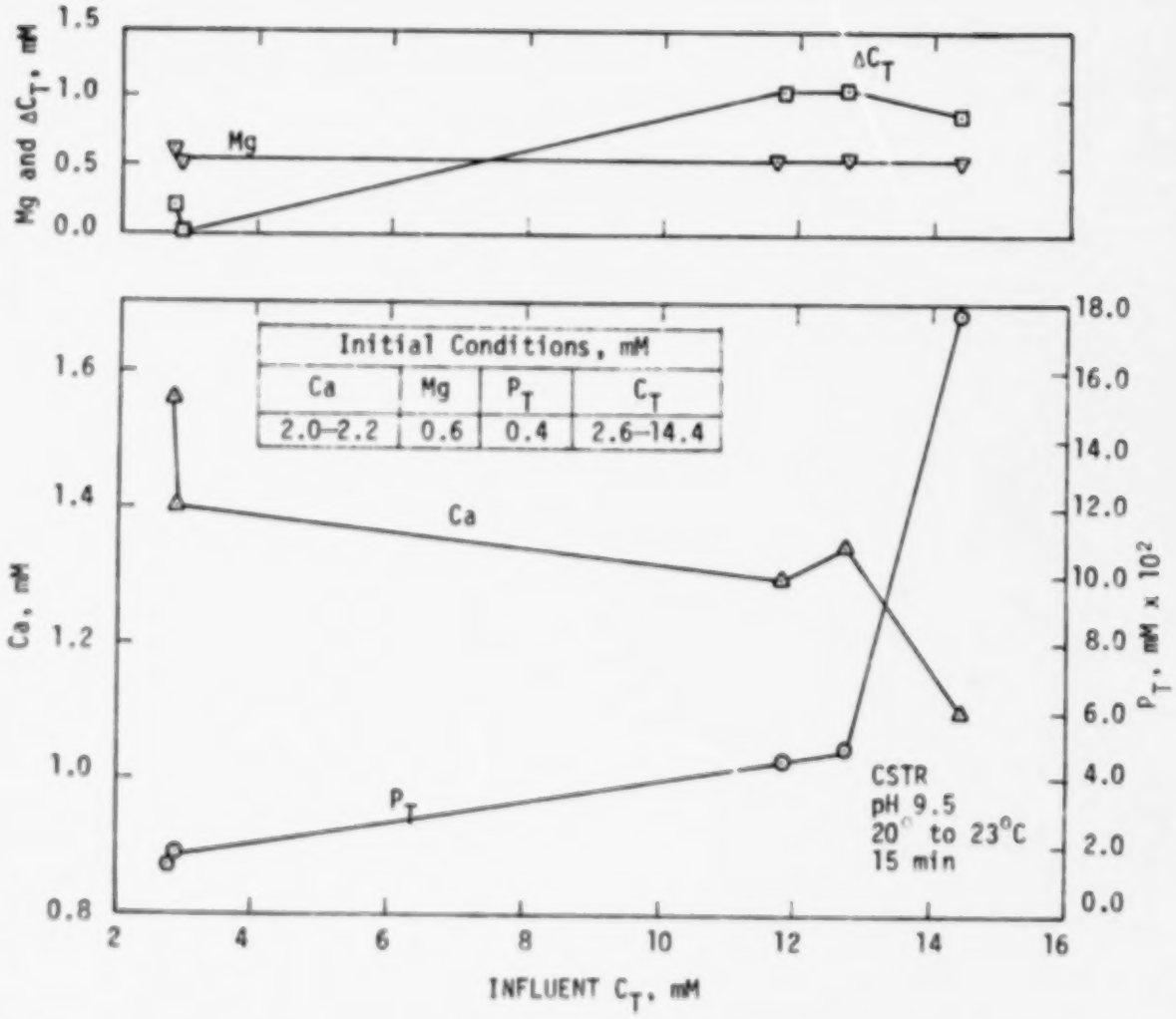


FIGURE 13. EFFECT OF C_T ON STEADY STATE CONCENTRATIONS OF Ca, Mg, AND P_T AND ON AMOUNT OF PRECIPITATED CARBONATE AT pH 9.5

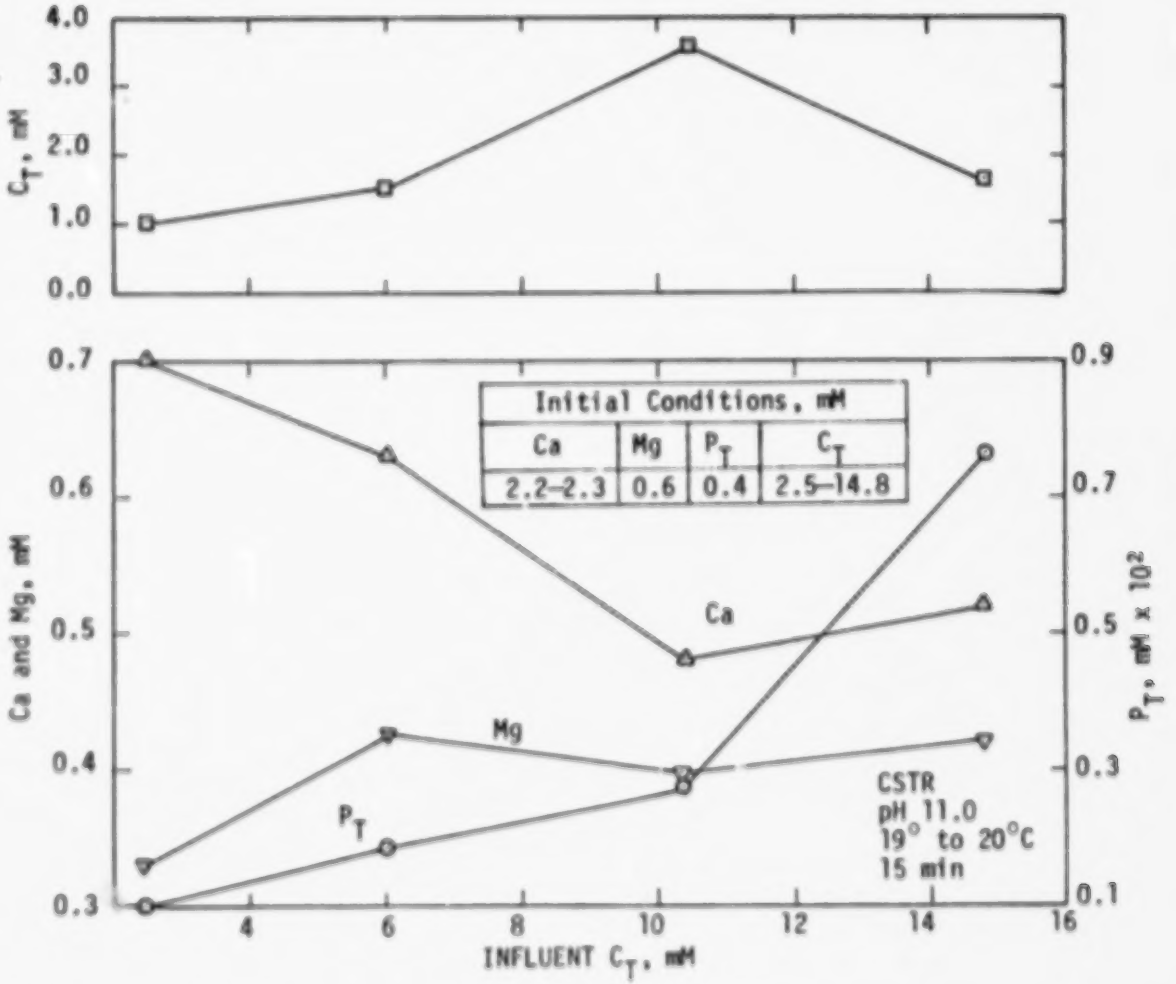


FIGURE 14. EFFECT OF C_T ON STEADY STATE CONCENTRATIONS OF Ca, Mg, AND P_T AND ON AMOUNT OF PRECIPITATED CARBONATE AT pH 11.0

At both pH values there is a very gradual increase in residual dissolved phosphate up to initial carbonate concentrations of 10 mM. Thereafter an extremely rapid increase in residual dissolved phosphate occurs at both pH values. These data are consistent then with the effects of carbonate on the activity product of TCP. Evidence exists from these data that carbonate is incorporated into the solids increasingly with increasing initial carbonate concentration. There is consistently higher carbonate incorporation into the solids at pH 11.0 than at pH 9.5 for all initial carbonate concentrations. Evidence that calcium carbonate precipitation occurred in both of these experiments is offered by additional CSTR data depicted in Figure 15. Here the ratio of Ca/P_T in the precipitate is plotted versus pH on the same graph as the C_T removed from solution. The curves have almost identical shapes and support the observation that

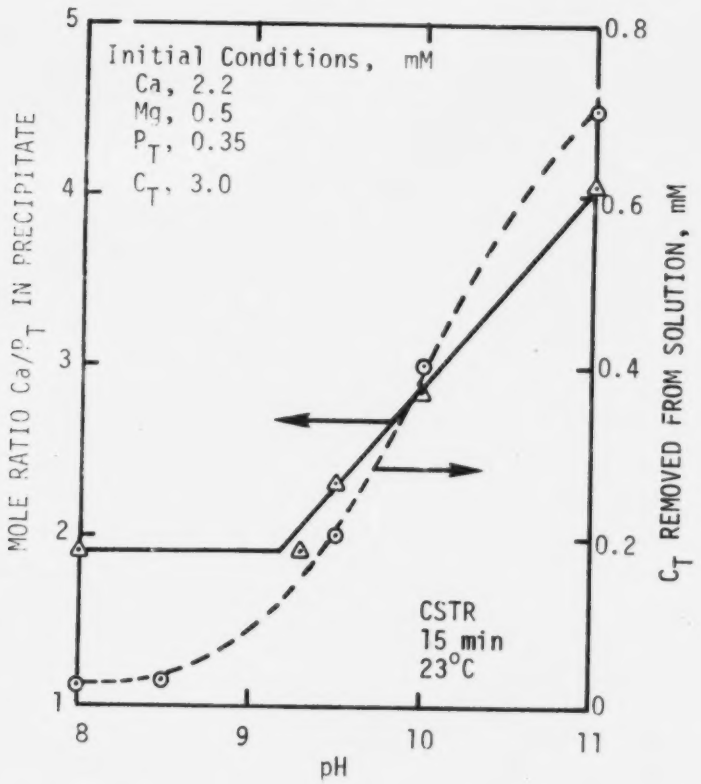


FIGURE 15. EFFECT OF pH ON Ca/P_T MOLE RATIO OF THE PRECIPITATE AND ON CARBONATE INCORPORATION INTO THE PRECIPITATE

calcium carbonate precipitation occurs at pH 9.5 and increasingly thereafter up to pH 11.0. These data also indicate that below pH 9.0 to 9.5 in systems with typical wastewater component concentrations, calcium carbonate precipitation is not significant.

Examination of the amount of carbonate and calcium removed from solution in these experiments suggests that more carbonate disappears from solution than can be accounted for by the precipitation of calcium carbonate (with a Ca/C_T mole ratio of 1). It must therefore be assumed, as has been indicated in the literature, that incorporation of the carbonate into the calcium phosphate solid occurs in such systems. This phenomenon has been reported to produce calcium phosphate solids whose solubility increases with their carbonate content. It is possible that the gradual increase of residual dissolved phosphate with increasing initial carbonate concentration, noted in Figures 12 and 13, and the gradual increase in TCP activity product, noted in Figure 11, is caused by carbonate inclusion in the calcium phosphate solid.

In these CSTR experiments Figures 13 and 14 demonstrate that for the entire range of initial carbonate concentrations and for both pH values of 9.5 and 11 there appears to be very little if any incorporation of magnesium into the solid.

It might be concluded then, that for the purpose of predicting dissolved phosphate residuals, the activity product of TCP derived in these experiments can be used satisfactorily for waters containing carbonate concentrations of below 4 mM (or alkalinities of below 400 mg $CaCO_3/\ell$) – values of alkalinity that are rarely exceeded in wastewaters.

METHOD OF PREDICTING DISSOLVED PHOSPHATE RESIDUAL

CSTR and batch experiments have shown that for the range of component concentrations commonly found in wastewaters, dissolved phosphate residuals may be predicted from the activity product of TCP as follows:

$$[Ca^{2+}]_{ss}^3 \; [PO_4^{3-}]_{ss}^2 = A \qquad (8)$$

where the subscript ss stands for steady state. The mean value for the negative logarithm of the activity product was determined to be 23.56. From a materials balance $[Ca^{2+}]_{ss}$ can be replaced by

$$[Ca^{2+}]_{ss} = \left\{[Ca^{2+}]_{in} - 1.5[P_{in} - P_{ss}]\right\} \qquad (9)$$

using the fact developed from Figure 9 that the Ca/P mole ratio of the precipitation approximates 1.5. Introducing a value of $10^{-23.56}$ for the

activity product and substituting Equation (9) into Equation (8) with the elimination of $[Ca^{2+}]_{ss}$, the logarithmic form of the equation becomes:

$$3 \log \left\{[Ca^{2+}]_{in} - 1.5\,[P_{in} - P_{ss}]\right\} + 2 \log [PO_4^{3-}] = -23.56 \ . \quad (10)$$

In this equation the only unknown is P_{ss}, the steady state concentration of total dissolved phosphate, since the value of PO_4^{3-} can be expressed as a function of pH, total dissolved phosphate, and equilibrium constants as follows:

$$[PO_4^{3-}]_{ss} = \frac{P_{ss}}{\left[1 + [H^+]/k_3 + [H^+]^2/k_2k_3 + [H^+]^3/k_1k_2k_3\right]} \quad (11)$$

where k_1, k_2, and k_3 are the first, second, and third equilibrium constants of phosphoric acid. Equation (10) can be solved manually for P_{ss} as illustrated in Appendix B.

Using this equation to predict phosphate residuals from the CSTR and batch experiments in chemically-defined systems gave excellent results (within 25% of experimental values) for systems with pH between pH 8 and 10, with initial magnesium up to 2 mM, and initial carbonate up to 4 mM (Table 6).

At pH 11.0 an error of 68% between predicted and experimental values was obtained for initial carbonate concentrations up to 3 mM. This error increased slightly (the predicted values were lower than experimental values) to the neighborhood of 73% when the initial carbonate concentration was increased to 6 mM. The increasing error in predicted values at both increased pH and carbonate concentration is undoubtedly caused by calcium carbonate precipitation which reduces the effective initial value of calcium. These errors were reduced so that predicted and experimental values of dissolved phosphate residual were within 25% when the precipitation of calcium carbonate was taken into consideration (Table 7).

CALCIUM PHOSPHATE PRECIPITATION AT pH 8 WITH SUSPENSION RECYCLE

As previously indicated, the calcium phosphate precipitation model of Stumm and Leckie [18] visualized precipitate formation in three steps — nucleation of an amorphous phase, phase transformation, and growth of a crystalline phase. In the short-term calcium phosphate precipitation processes examined in the previous part of this chapter it was postulated that the solid present in the phase transformation step would control the

TABLE 6

COMPARISON OF PREDICTED AND EXPERIMENTAL RESIDUAL PHOSPHATE VALUES IN CHEMICALLY-DEFINED SYSTEMS

pH	pA $Ca_3(PO_4)_2$ Range		Dissolved P_T, mM x 10^4		Error[a] %
			Experimental	Predicted	
8.0	High	22.92	2100	1000	-57.2
	Low	24.35	4200	1300	-69.0
	Mean	23.69	4500	4280	- 4.4
9.0	High	22.80	1200	500	-58.4
	Low	23.68	620	530	-14.5
	Mean	23.49	550	500	- 9.1
9.5	High	22.96	280	185	-34.0
	Low	24.08	110	177	+60.7
	Mean	23.71	34	31	- 8.8
10.0	High	22.77	130	43	-67.0
	Low	24.03	230	222	+ 3.5
	Mean	23.74	48	52	+ 8.3
11.0	High	22.44	94	13.5	-85.6
	Low	24.44	3.3	5.1	+54.6
	Mean	23.55	6.5	6.4	- 1.5

[a] $\%\ \text{Error} = \frac{P - E}{E} \times 100.$

dissolved phosphate residual. It was found that at residence times typical of the processes this steady state solid has the characteristics of an amorphous tricalcium phosphate.

There is considerable evidence [3,4,18] that the phase transformation step can be shortened (or even eliminated) by the presence of preformed crystalline material in the precipitating medium. Indeed the reported

TABLE 7

COMPARISON OF PREDICTED AND EXPERIMENTAL RESIDUAL PHOSPHATE VALUES IN CHEMICALLY-DEFINED SYSTEMS CORRECTED FOR CALCIUM CARBONATE PRECIPITATION

pH	C_T mM	Dissolved P_T, mM x 10^4			Error[a], %	
		Predicted		Experimental	Uncorrected for $CaCO_3$ Precipitation	Corrected for $CaCO_3$ Precipitation
		Uncorrected for $CaCO_3$ Precipitation	Corrected for $CaCO_3$ Precipitation			
11.0	1.5	5.16	3.90	3.23	+60	+22
11.0	3.0	5.16	14.1	16.1	-68	-13
11.0	6.0	5.11	13.4	18.7	-73	-25

[a] Error = $\frac{P - E}{E} \times 100$.

success of the Phosphate Extraction Process [16], in which precipitated solids are recycled, is attributed to providing a high concentration of solids to encourage more rapid crystal growth of calcium phosphate. Because of these observations, a limited investigation was conducted on chemically-defined systems to determine the feasibility of obtaining low phosphate residuals at pH 8 through the recycle of preformed precipitate.

Two CSTR experiments, each of about 2 weeks duration, were conducted using a single CSTR followed by a sedimentation basin from which settled suspension could be recycled to the CSTR (Figure 3).

In the first experiment an attempt was made to build up precipitate by recycling sedimentation basin underflow from a solution containing the following initial component concentrations: Ca, 2.2 mM; Mg, 0.5 mM; P_T, 0.3 mM; C_T, 3.2 mM; pH 8. After a period of 13 days it became evident that it would not be possible to build up a high precipitate level in the reactor because of the poor settling characteristics of the precipitate. Indeed, throughout the almost two weeks of continuous operation the reactor suspension concentration did not exceed 6 mg/ℓ and no significant phosphate removal was achieved.

In the second experiment an aged calcium phosphate–carbonate suspension was preformed in the reactor by adding 3 ℓ, 10 M $CaCl_2$ solution to 10 ℓ

distilled water followed by 750 mℓ conc. H_3PO_4 and then sufficient 50% NaOH solution to achieve a pH of 8. After aging the stirred suspension for 2 days the CSTR was continuously fed with a solution whose initial composition was: Ca, 2.2 mM; Mg, 0.5 mM; P_T, 0.3 mM; C_T, 3.2 mM; pH 8.2. Settling problems were again encountered and the initial suspension concentration of 5900 mg/ℓ fell rapidly during the first 2 days of operation to a level of approximately 1500 to 2000 mg/ℓ. Over the one week period that suspension concentrations of 1500 to 2000 mg/ℓ were maintained, it was possible to remove 60% of the incoming phosphate. Following this period of operation, continuing difficulties in suspension separation caused a further decrease in reactor suspension concentration to about 50 mg/ℓ at the termination of the experiment (Figures 16 and 17). At this time the dissolved phosphate removal had decreased to 20%.

At the same time that these CSTR experiments were proceeding, batch experiments were conducted on solutions of identical composition to the CSTR feed. Suspension from the CSTR reactor was introduced into two 4-ℓ beakers containing CSTR feed solution to achieve initial levels of 3 and 3000 mg/ℓ suspension, respectively. The batch reactors were stirred for 29 hr. Figure 18 shows that the dissolved phosphate concentration in the high suspension concentration reactor decreased more rapidly and to a lower level than the dissolved phosphate concentration in the low suspension concentration reactor. A further illustration that the presence of calcium carbonate-phosphate suspension enhances phosphate removal was provided by a series of experiments in which solutions of composition identical to the CSTR feed were filtered through layers of suspension taken from the CSTR reactor that had been deposited on the surface of membrane filters in a 2-cm deep bed. When the filtrate composition was analyzed for phosphate it was revealed that one passage of CSTR feed solution through such a precipitate bed effected a 54% removal of phosphate; this was increased by successive refiltrations to 56% and 60% removal. These results are of significance because the conditions in such a refiltration experiment might be thought of as being somewhat similar to those existing in the sludge blanket of an upflow clarifier. It might be surmised that such an expanded bed of precipitate could have many of the important features (albeit with a lower residence time) of a reactor to which precipitate is recycled.

X-ray powder diffraction analysis of the suspensions from continuous, batch, and refiltration experiments provided an important piece of evidence in support of the postulate that the steady state solid was a tricalcium phosphate. The presence of $Ca_3(PO_4)_2 \cdot nH_2O$ was detected by these analyses and by chemical analysis of the solid. The value of n was found to be 4.

The effect of recycled solids concentration on the activity product of TCP is shown in Figure 19. The close correlation between activity product and suspended precipitate concentration serves to emphasize the catalytic effect of solids in the formation of more insoluble phases.

These experiments clearly indicate that low phosphate residuals can be achieved at pH 8 from waters with a mineral composition typical of many

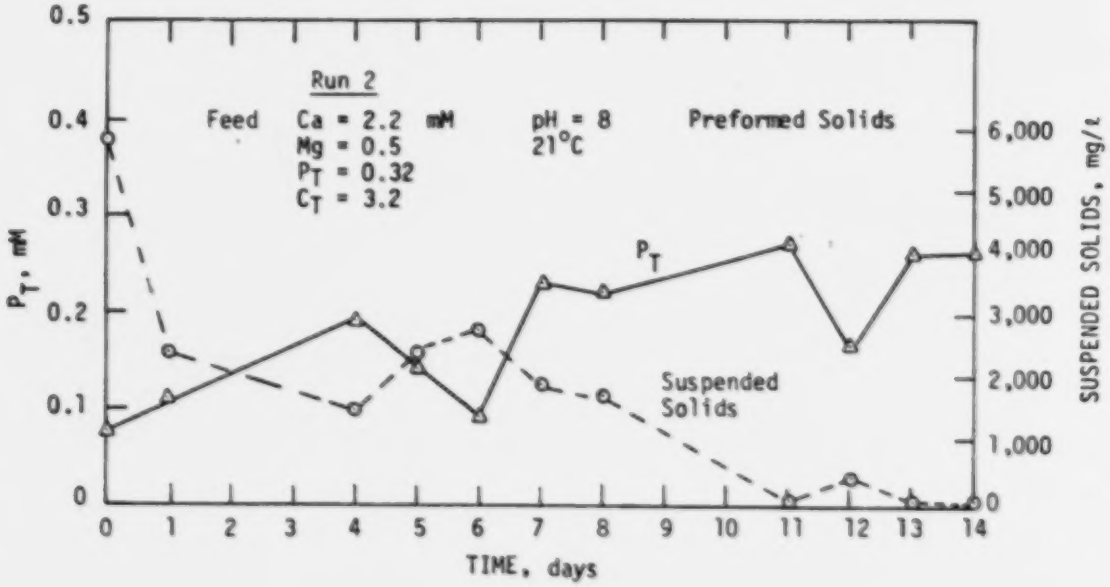


FIGURE 16. EFFECT OF SUSPENSION CONCENTRATION ON EFFLUENT PHOSPHATE CONCENTRATION IN PRECIPITATE RECYCLE EXPERIMENTS

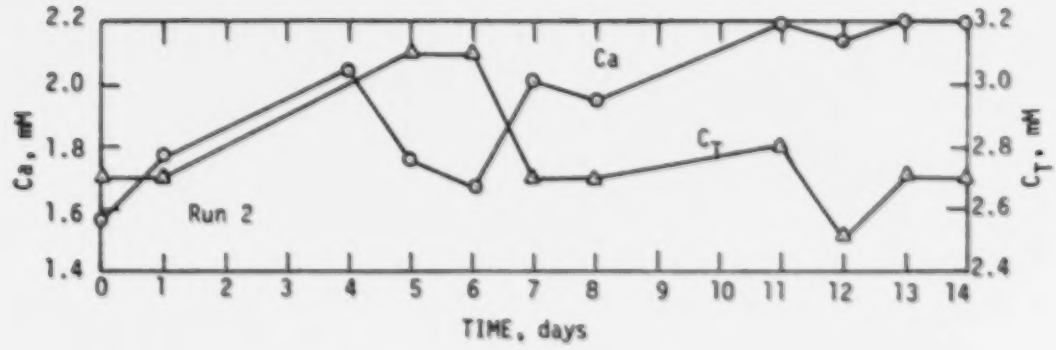


FIGURE 17. STEADY STATE Ca AND C_T CONCENTRATIONS DURING PRECIPITATE RECYCLE EXPERIMENTS

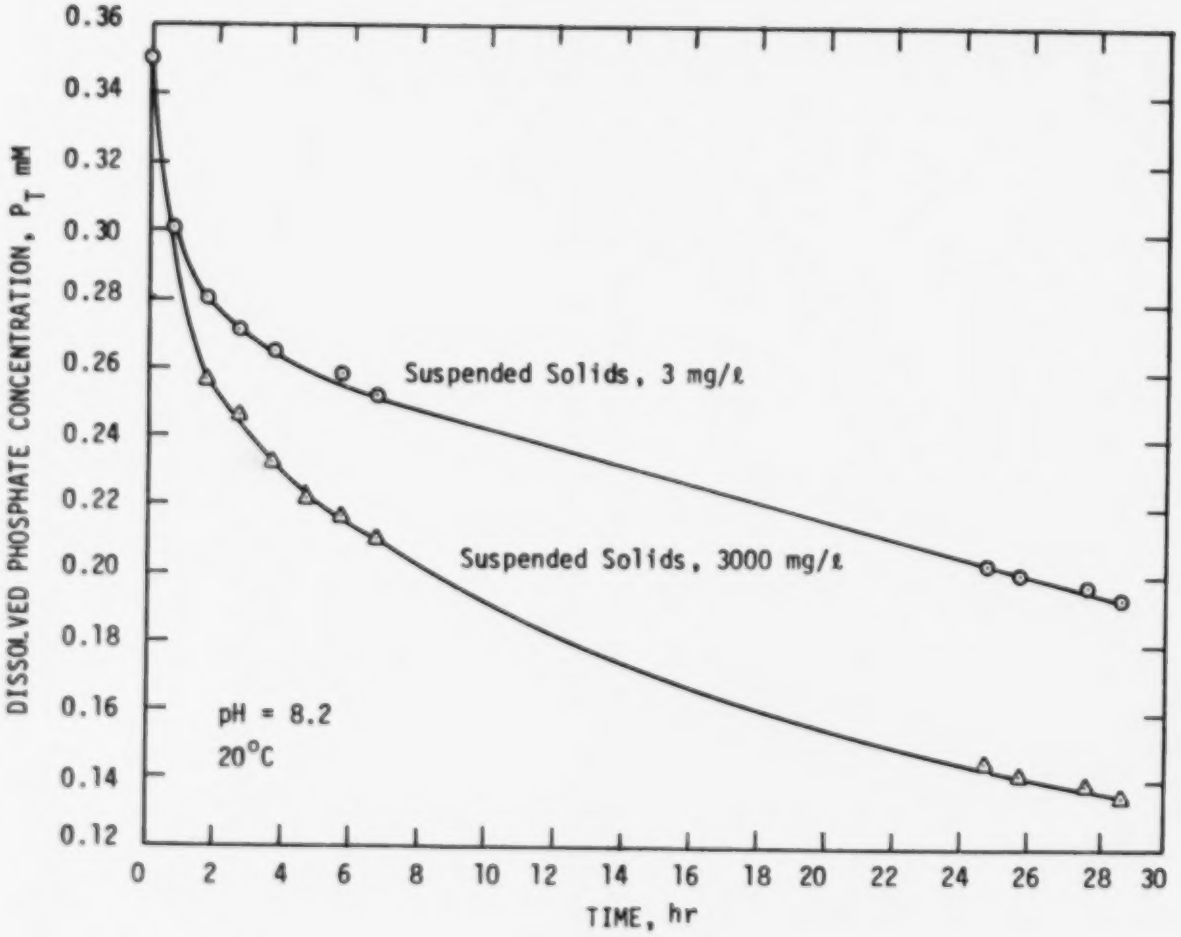


FIGURE 18. EFFECT OF SUSPENSION CONCENTRATIONS ON RATE OF CALCIUM PHOSPHATE PRECIPITATION IN BATCH EXPERIMENTS

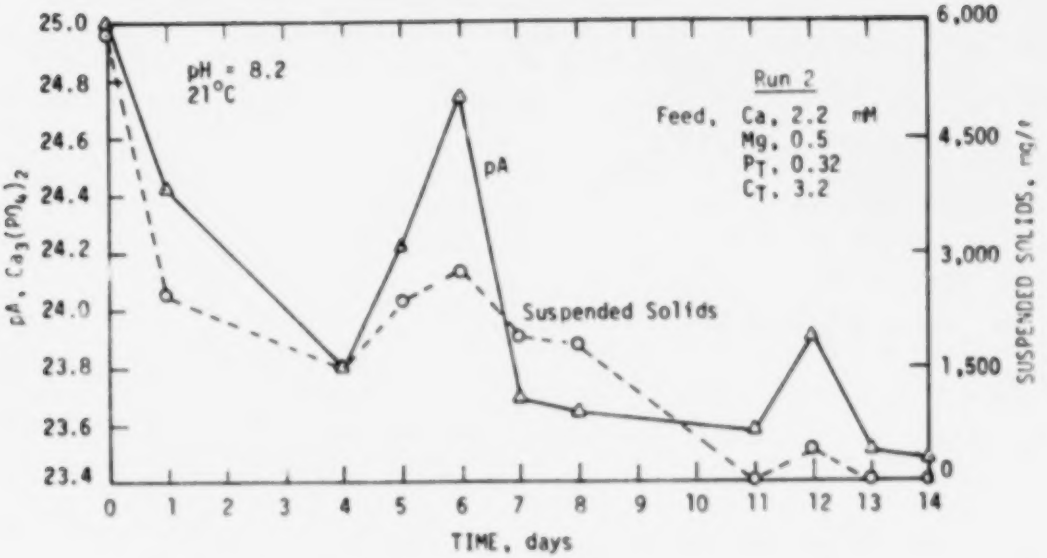


FIGURE 19. EFFECT OF SUSPENSION CONCENTRATION ON pA $Ca_3(PO_4)_2$ IN PRECIPITATE RECYCLE EXPERIMENTS

domestic wastewaters by the use of precipitate recycle to produce high suspension concentrations for calcium phosphate crystal growth. The experiments also emphasize the importance of precipitate separation in calcium phosphate precipitation processes and the absolute necessity for development of methods to enhance the settling properties of the calcium phosphate–carbonate suspensions produced at pH values below 10.

SECTION IX

PRECIPITATION OF PHOSPHATE IN WASTEWATER

Five series of phosphate precipitation experiments were conducted on wastewater in the SERL wastewater treatment facility. Each experimental run lasted for at least 4 days. In the first four experiments the phosphate removal performance of each individual unit of the entire treatment train was examined, including primary sedimentation, activated sludge, lime precipitation, recarbonation, and clinoptilolite sorption. In the fifth experimental run the phosphate removal performance of a lime precipitation unit operating on the primary effluent was assessed.

OVERALL PHOSPHATE REMOVAL PERFORMANCE

The phosphate removal performance over the entire experimental period for the whole process train is summarized in Figure 20. Performance data are given for actual phosphate removal as well as maximum possible phosphate removal — i.e., the removal of phosphate that would occur if perfect separation of particulates were possible.

Daily experimental values derived from 24-hr composite samples for pH, Ca, Mg, alkalinity and dissolved and total phosphate are presented in Appendix C. Mean values of these parameters, together with the mean values of imposed operating conditions, are presented in Tables 8 through 12.

In experiment 1 lime slurry was added to activated sludge effluent and precipitation conducted in a 3-compartment mixer-flocculator with nominal residence time of 46.5 min in a run of 8 day's duration. Lime doses of 2.9 mM (290 mg as $CaCO_3$/ℓ) raised the pH of the activated sludge effluent feed from 7.2 to 10.8 and reduced the total phosphate from an average influent value of 11.1 mg P/ℓ to a residual of 0.5 mg P/ℓ in the effluent from the clinoptilolite column (Table 8). In this experiment, as was the case in all of the wastewater runs, the dissolved phosphate concentration leaving the clarifier following the precipitation unit was lower than that following recarbonation. In this experiment, average dissolved phosphate levels of 0.12 mg P/ℓ were present in the settled effluent from precipitation while the dissolved phosphate following recarbonation of this effluent was 0.50 mg P/ℓ. Subsequent experiments showed that virtually all of the particulate phosphate that escaped sedimentation redissolved in the lower pH medium of the recarbonation basin within the 5-min average detention time of this basin. Indeed, following recarbonation only an insignificant fraction of the phosphate was present in the effluent as particulate matter. It is this factor that accounts for the observation

Preceding page blank

TABLE 8

OPERATING CONDITIONS AND RESULTS FOR WASTEWATER
EXPERIMENT 1

Sample Location	P		Ca	Mg	C_T	Alkalinity	pH
	Total mM	Dissolved mM	Dissolved mM	Dissolved mM	Dissolved mM	Dissolved mM	
Primary Effluent	0.37	0.31	1.38	0.37	-	2.65	7.4
Activated Sludge Effluent	0.36	0.30	1.39	0.37	1.97	0.85	7.2
Lime Precipitation Effluent	-	0.00389	1.93	0.26	0.67	1.50	10.8
Recarbonation Effluent	-	0.016	-	0.26	-	1.75	8.5
Clinoptilolite Effluent	0.017	0.016	1.72	0.25	-	1.76	8.5

Feed to precipitation unit: Activated sludge effluent; Number of compartments: 3; Nominal residence time: 46.5 min; Total lime added: 2.9 mM, Dissolved lime added: 0.1 mM.

TABLE 9

OPERATING CONDITIONS AND RESULTS FOR WASTEWATER
EXPERIMENT 2

Sample Location	P		Ca	Mg	C_T	Alkalinity	pH
	Total mM	Dissolved mM	Dissolved mM	Dissolved mM	Dissolved mM	Dissolved mM	
Primary Effluent	0.39	-	1.36	0.42	-	2.48	7.4
Activated Sludge Effluent	0.35	0.34	1.37	0.41	2.10	0.84	7.3
Lime Precipitation Effluent	0.053	0.0184	1.76	0.36	1.95	1.77	9.8
Recarbonation Effluent	0.056	0.053	1.72	0.36	-	1.79	8.2
Clinoptilolite Effluent	0.056	0.054	1.14	0.37	-	1.78	8.4

Feed to precipitation unit: Activated sludge effluent; Number of compartments: 3; Nominal residence time: 46.5 min; Total lime added: 1.6 mM; Dissolved lime added: 0.1 mM.

TABLE 10

OPERATING CONDITIONS AND RESULTS FOR WASTEWATER EXPERIMENT 3

Sample Location	P		Ca Dissolved mM	Mg Dissolved mM	C_T Dissolved mM	Alkalinity Dissolved mM	pH
	Total mM	Dissolved mM					
Primary Effluent	0.37	0.28	1.20	0.38	3.8	2.35	7.4
Activated Sludge Effluent	-	-	-	-	-	-	-
Lime Precipitation Effluent	0.0089	0.00323	1.51	0.24	0.6	2.46	11.0
Recarbonation Effluent	0.0076	0.007	1.90	0.26	-	2.94	7.7
Clinoptilolite Effluent	0.0076	0.007	1.41	0.26	5.0	2.97	7.8

Feed to precipitation unit: Primary effluent; Number of Compartments: 3; Nominal residence time: 46.5 min; Total lime Added: 4.9 mM; Dissolved lime added: 0.2 mM.

TABLE 11

OPERATING CONDITIONS AND RESULTS FOR WASTEWATER EXPERIMENT 4

Sample Location	P		Ca Dissolved mM	Mg Dissolved mM	C_T Dissolved mM	Alkalinity Dissolved mM	pH
	Total mM	Dissolved mM					
Primary Effluent	0.35	0.28	1.10	0.37	3.2	-	7.4
Activated Sludge Effluent	-	-	-	-	-	-	-
Lime Precipitation Effluent	0.018	0.0074	1.07	0.31	1.4	-	10.2
Recarbonation Effluent	0.027	0.023	1.26	0.30	4.0	-	-
Clinoptilolite Effluent	0.021	0.019	1.24	0.33	4.3	-	-

Feed to precipitation unit: Primary effluent; Number of compartments: 3; Nominal residence time: 46.5 min; Total lime added: 2.8 mM; Dissolved lime added: 0.1 mM.

TABLE 12

OPERATING CONDITIONS AND RESULTS FOR WASTEWATER EXPERIMENT 5

Sample Location	P		Ca Dissolved mM	Mg Dissolved mM	C_T Dissolved mM	Alkalinity Dissolved mM	pH
	Total mM	Dissolved mM					
Primary Effluent	0.40	0.33	1.40	0.42	3.60	2.46	7.5
Activated Sludge Effluent	-	-	-	-	-	-	-
Lime Precipitation Effluent	0.026	0.019	1.71	0.36	3.00	3.06	9.6
Recarbonation Effluent	-	-	-	-	-	-	-
Clinoptilolite Effluent	-	-	-	-	-	-	-

Feed to precipitation unit: Primary effluent; Number of compartments: 4; Nominal residence time: 42 min; Total lime added: 2.6 mM; Dissolved lime added: 0.2 mM.

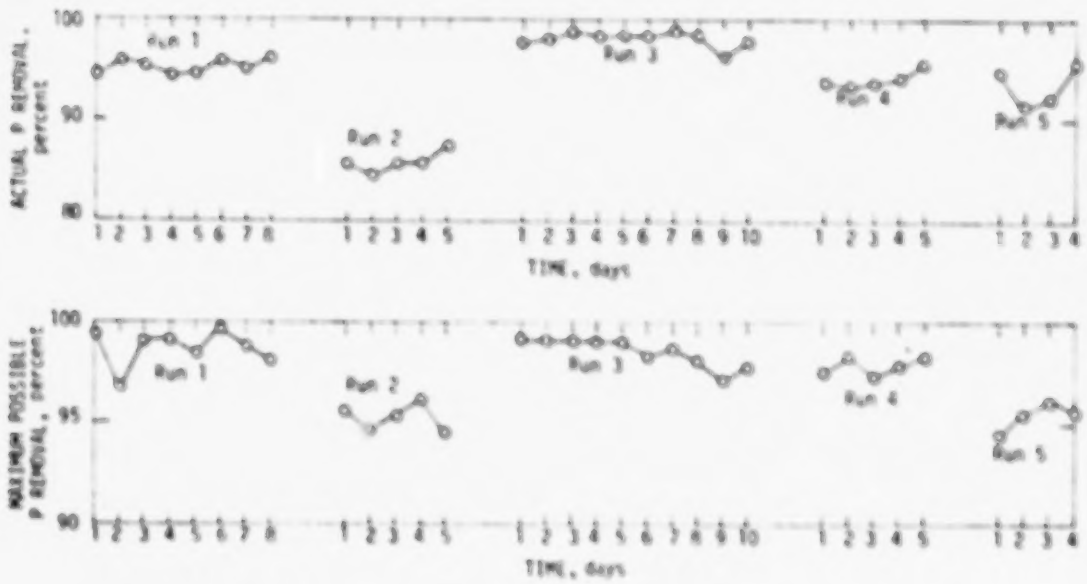


FIGURE 20. PHOSPHORUS REMOVAL PERFORMANCE OF THE ENTIRE PROCESS TRAIN DURING PILOT PLANT RUNS ON WASTEWATER

than no phosphate removal was effected by the clinoptilolite columns – since removal by these columns can only be expected by filtration and filtration is only effective in removing particles.

In experiment 2 activated sludge effluent was treated with lime in a 3-compartment mixer-flocculator with average nominal residence time of 46.5 min for an experimental period of 5 days. Lime doses of 1.6 mM (160 mg as $CaCO_3/\ell$) raised the pH of the activated sludge effluent from 7.3 to 9.8 and reduced the influent total phosphate from 10.8 mg P/ℓ to a value of 1.7 mg P/ℓ following treatment by the whole process stream including recarbonation and clinoptilolite columns (Table 9). Dissolution of particulate phosphate occurred during recarbonation (causing an increase in dissolved phosphate from 0.6 mg P/ℓ to 1.7 mg P/ℓ) as the pH was reduced from 9.8 to 8.2.

In experiment 3 primary effluent was treated in a 3-compartment mixer-flocculator with average nominal residence time of 46.5 min for an experimental period of 10 days. Lime doses of 4.9 mM (490 mg as $CaCO_3/\ell$) raised the pH of the primary effluent to 11.0 and reduced total phosphate from a value of 11.5 mg P/ℓ to a residual of 0.23 mg P/ℓ following the process stream of recarbonation and clinoptilolite treatment (Table 10). Recarbonation resulted in an increase of dissolved phosphate from 0.1 mg P/ℓ to about 0.2 mg P/ℓ as the pH was adjusted downward from 11.0 to 7.7.

In run 4 the experimental conditions were similar to those used in experiment 3 with the exception that, over a five-day period, primary effluent was dosed with 2.8 mM lime (280 mg as $CaCO_3/\ell$) to reach a precipitation pH of 10.2. Final process total phosphate levels averaged 0.65 mg P/ℓ – levels that were increased by recarbonation from the 0.56 mg P/ℓ achieved following sedimentation of the precipitated effluent.

In the final wastewater precipitation experiment (experiment 5) primary effluent was treated in a 4-compartment mixer-flocculator with an average residence time of 42 min for an experimental period of 4 days. At the precipitation pH of 9.6, achieved by a lime dose of 2.6 mM (260 mg as $CaCO_3/\ell$), the precipitation-sedimentation unit reduced the total phosphate from 12.4 mg P/ℓ to 0.81 mg P/ℓ.

COMPARISON OF PREDICTED AND EXPERIMENTAL PHOSPHATE RESIDUALS

Good prediction of effluent dissolved phosphate concentration using Equation (10) derived from the precipitation model developed from chemically-defined solutions was obtained when based on the concentrations of dissolved constituents and with corrections being made for complexing of calcium and for calcium carbonate precipitation. This procedure was made necessary largely by the extremely poor efficiency of lime dissolution obtained in the pilot plant. Thus Figure 21 indicates that of the lime added to the lime dissolution unit some amount on the order of 10% or

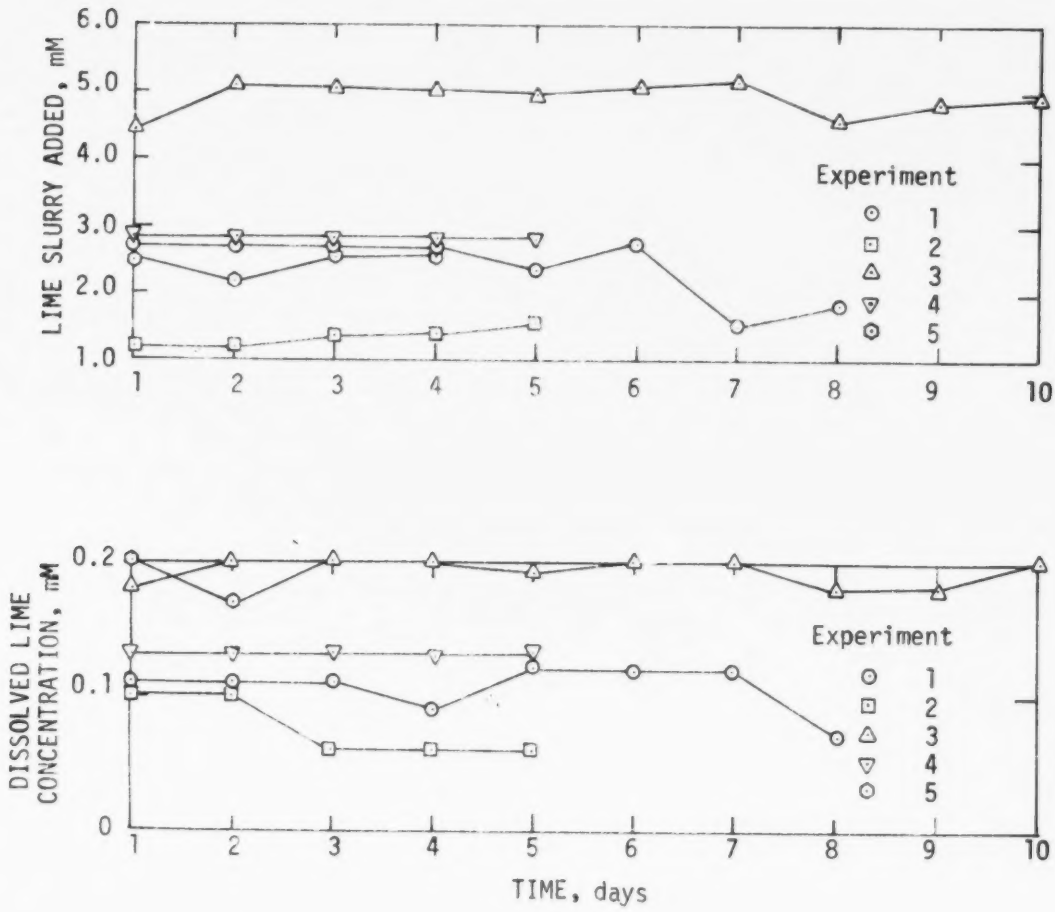


FIGURE 21. COMPARISON OF LIME SLURRY ADDITION TO DISSOLVED LIME CONCENTRATION IN WASTEWATER EXPERIMENTS

less became dissolved in the wastewater in the first compartment of the precipitation reactor. Additional complications arose because the lime continued to dissolve in the subsequent reactor compartments. Thus Figure 22 shows the increase in dissolved calcium caused by lime dissolution as one progresses down the precipitation reactors.

When the dissolved calcium concentration was used the model produced predictions of dissolved phosphate residuals that were within 25% of experimental values (Table 13). Previous attempts to predict residual

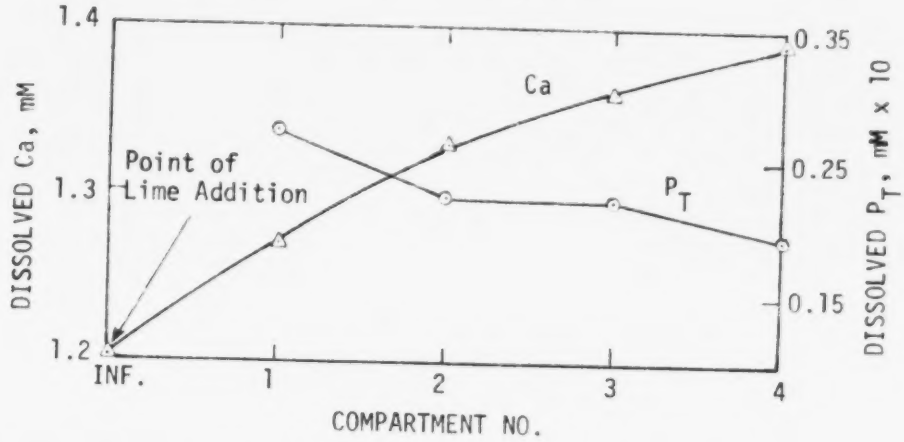


FIGURE 22. CHANGE IN DISSOLVED Ca AND P_T CONCENTRATIONS IN REACTOR COMPARTMENTS – WASTEWATER EXPERIMENTS

phosphate concentrations in wastewater as a result of chemical dosing have been in error by a factor of some 5 times [3].

TABLE 13

COMPARISON OF PREDICTED AND AVERAGE EXPERIMENTAL DISSOLVED PHOSPHATE RESIDUALS FOR WASTEWATER EXPERIMENTS

Experiment No.	Dissolved Phosphate Residual, mM x 10^4		Error[a] %
	Predicted	Experimental	
1	47.5	38.9	+22
2	208	184	+13
3	36.2	32.3	+17
4	92.2	74.0	+25
5	230	190	+21

[a] $\% \text{ Error} = \frac{\text{Predicted} - \text{Experimental}}{\text{Experimental}} \times 100.$

Figure 23 shows the variation of the activity product of TCP with pH in comparison with the values of this constant from chemically-defined systems. In computing the activity product of TCP for wastewaters the complexing of calcium was taken into account (Appendix B). The line for the wastewater points was fitted by least squares analysis. The agreement between the values of this constant from the two types of system is good at pH values below 10.5. At higher pH values the pA value of TCP in the wastewater systems (where lime was used as a precipitant) is significantly lower than for chemically-defined systems where dissolved calcium salts were used as precipitants.

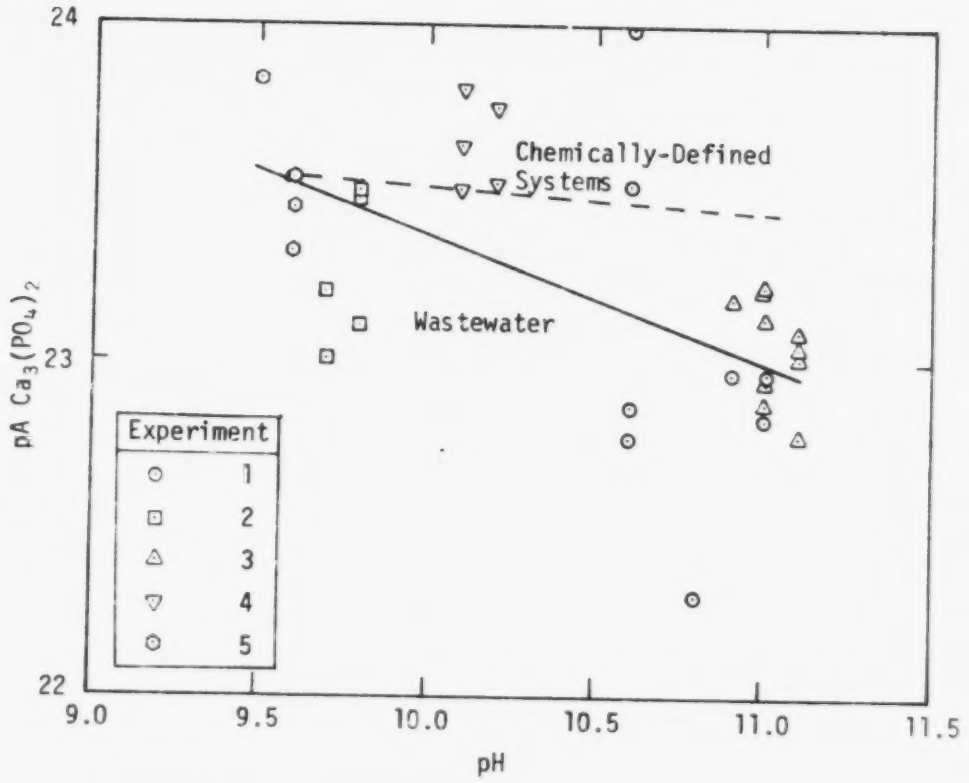


FIGURE 23. DEPENDENCE OF pA $Ca_3(PO_4)_2$ ON pH FOR WASTEWATER EXPERIMENTS

OVERALL PHOSPHATE REMOVAL PERFORMANCE

In the wastewater tested(which is one with an average alkalinity of 2.4 mM and a typical Ca/Mg mole ratio of approximately 3 to 1), a phosphate removal in excess of 80% was consistently achieved at pH 9.5 with lime doses of, at the most, 2 mM (200 mg/ℓ as $CaCO_3$). Indeed, for most of

the experimental period phosphate removals exceeded 90%. It should be noted, however, that the overall phosphate removal performance (total rather than the removal based on dissolved phosphate concentration) of the entire treatment train was dictated by the performance of the precipitation reactor and its ensuing sedimentation basin. It was demonstrated that any phosphate-containing particles that escaped sedimentation were rapidly dissolved during recarbonation (Tables 8 through 12). This observation raises the important issue of the efficacy of filtration for improving the phosphate removal for wastewater treated by lime precipitation. Effluents from all such processes will require downward pH adjustment by some process such as recarbonation prior to filtration. As these experiments have demonstrated, however, even short-term (5 min) recarbonation or other low pH environments will cause the rapid and complete dissolution of the particulate phosphate, thus making it non-removable by filtration. It must be concluded, therefore, that filtration cannot be used to reduce the phosphate residual in lime-treated wastewater and that the effective phosphate residual of a lime precipitation phosphate removal process is determined by the efficiency of the sedimentation process following precipitation.

Because of this observation, which emphasized the importance of precipitate removal by sedimentation, some preliminary experiments were conducted on chemically-defined systems to investigate the effect of solution composition on the behavior of calcium phosphate–carbonate suspensions during sedimentation.

Factors Influencing Separation of Precipitates

Previous literature has attributed the inability to operate calcium phosphate precipitation processes efficiently below pH values in the 10.5 to 11 region to the production of poorly flocculated precipitates that cannot be readily separated. Operation of these processes at pH values of 10.5 or greater was thought to be beneficial from a precipitate separation standpoint because of the formation of $CaCO_3$ (which supposedly increases suspension density) and of $Mg(OH)_2$ (which reportedly is gelatinous and acts as a suspension binder).

Two series of CSTR experiments were conducted on chemically-defined solutions with the objective of determining the effect of precipitating conditions on the settling properties of the precipitates that were formed. Variables investigated included pH; initial concentrations of calcium, magnesium, and carbonate; and the initial Ca/Mg ratios. Both series of experiments employed single CSTR's at 23°C, with 15 min nominal residence time and with mean velocity gradient values of 76 sec^{-1}. The settling properties of the suspension were assessed by quiescent sedimentation for 30 min following the CSTR. Initial component concentrations for the two series of experiments are presented in Tables 14 and 15.

Of the variables studied, initial magnesium concentration and pH exerted the most influence on the separation by sedimentation of calcium

TABLE 14

INITIAL COMPONENT CONCENTRATION FOR PRECIPITATE SEPARATION EXPERIMENTS, SERIES I

Run No.	Ca mM	Mg mM	P_T mM	C_T mM	pH (Range of Variation)	Ca/Mg Mole Ratio	Ca/C_T Mole Ratio	Ca/P_T Mole Ratio
1	14.2	3.7	0.4	2.4	8 –11	3.8	5.9	4 0
2	2.2	0.6	0.4	2.4	8 –11	3.7	0.9	6.1
3	2.2	3.6	0.4	2.6	8.5–10.9	0.6	0.8	6.1
4	2.2	10.8	0.4	2.4	8.5–11	0.2	0.9	6.0

TABLE 15

INITIAL COMPONENT CONCENTRATION FOR PRECIPITATE SEPARATION EXPERIMENTS, SERIES II

Run No.	Ca mM	Mg mM	P_T mM	C_T mM (Range of Variation)	pH	Ca/Mg Mole Ratio	Ca/C_T Mole Ratio (Range of Variation)	Ca/P_T Mole Ratio
1	2.2	0.6	0.4	2.7–12.7	9.0	3.7	0.2–0.8	6.1
2	2.2	0.6	0.4	2.7–12.7	9.5	3.7	0.2–0.8	6.1
3	2.2	0.6	0.4	2.7–12.7	10.0	3.7	0.2–0.8	6.1
4	2.2	0.6	0.4	2.7–12.7	11.0	3.7	0.2–0.8	6.1

phosphate–carbonate suspensions. Examination of Figures 24 and 25 shows that increasing the pH of suspensions in general improved their settling characteristics. Indeed, if one were to select the very modest criterion that 90% removal of precipitate by sedimentation was the minimum acceptable performance for a precipitate separation process, then only operation at a pH value of greater than 10.5 would consistently achieve this objective. In the pH range between 8 and 10 the suspensions generally settled poorly. The influence of magnesium concentration on suspension settling is

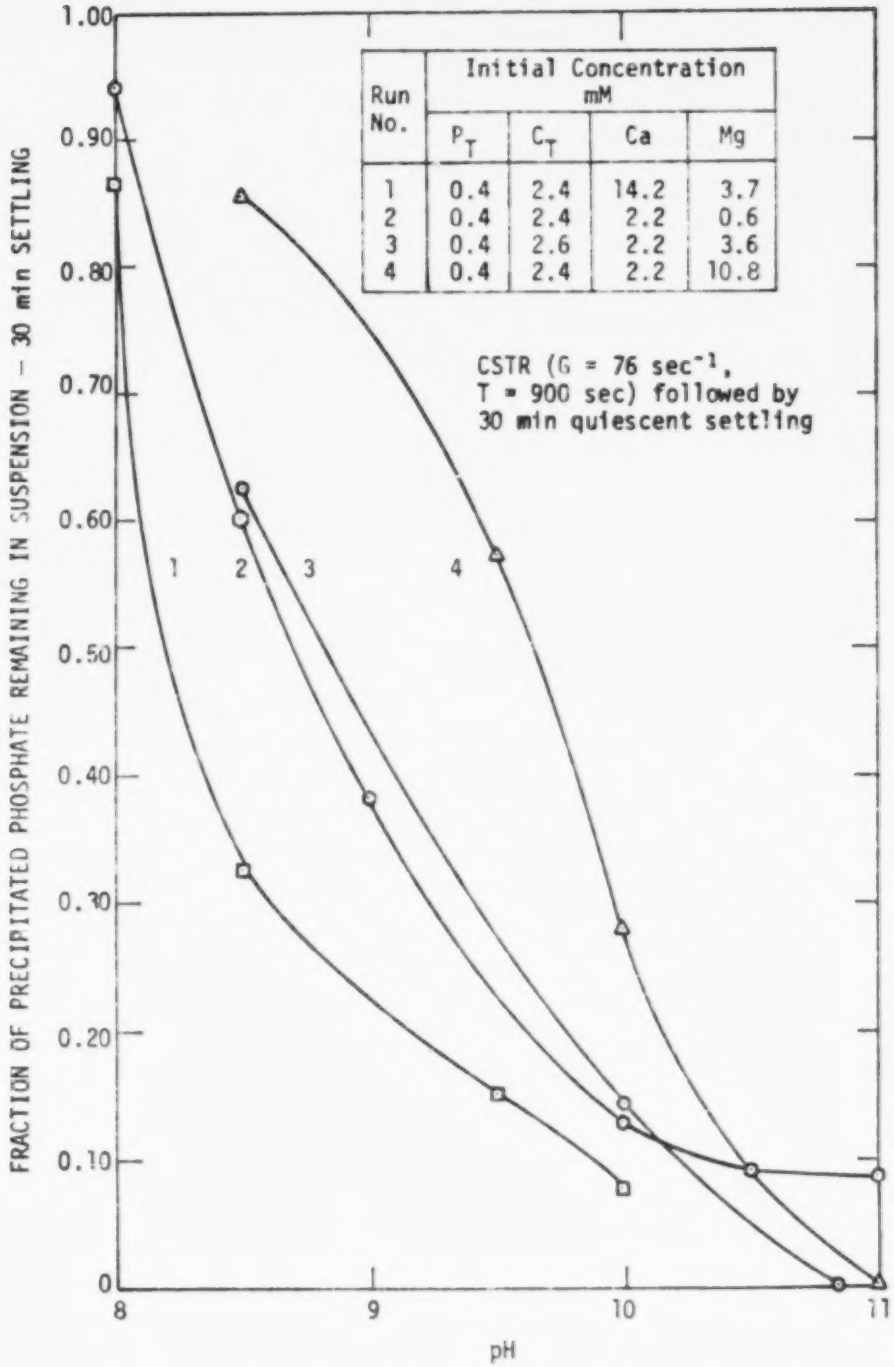


FIGURE 24. SETTLING PROPERTIES OF CALCIUM PHOSPHATE-CARBONATE SUSPENSIONS (SERIES I)

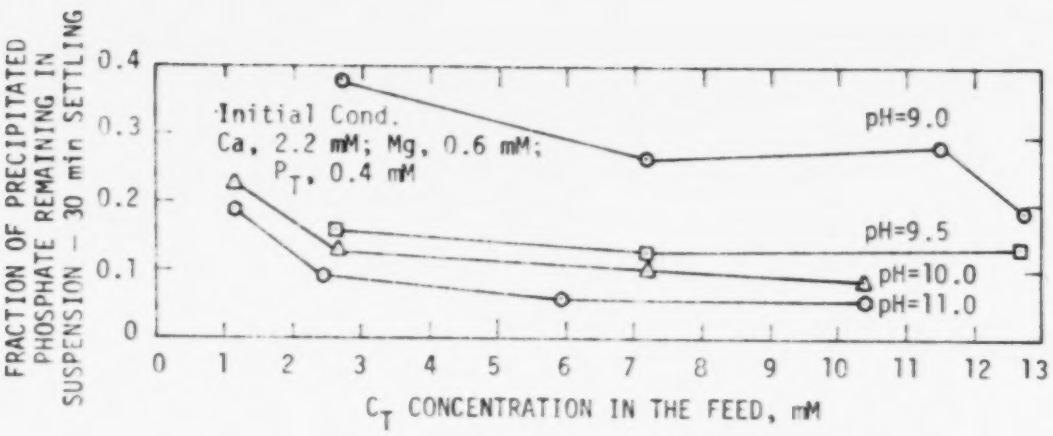


FIGURE 25. SETTLING PROPERTIES OF CALCIUM PHOSPHATE-CARBONATE SUSPENSIONS (SERIES II)

exerted most evidently at pH values greater than 10.5 where precipitation of gelatinous $Mg(OH)_2$ is likely. In the pH range 8 to 10 increasing Mg concentration (or decreasing Ca/Mg ratio) had a deleterious effect on suspension settling only at very high magnesium concentrations -- concentrations unlikely to be encountered in a wastewater. Thus, when the influent magnesium was increased from 0.6 to 3.6 mM (with all other constituents constant) no noticeable effect on phosphate removal of particulate phosphate by sedimentation was observed over the pH range from 8 to 10 (Figure 24, Runs 2 and 3). However, increasing magnesium concentration to 10.8 mM and thereby decreasing the Ca/Mg mole ratio to 0.2 had a markedly deleterious effect on phosphate removal by sedimentation (Figure 24, Run 4).

Previous statements in the literature suggesting that calcium carbonate precipitation aids precipitate separation by producing a dense suspension were not supported by this investigation. Increases of initial calcium concentrations from 2.2 to 14.2 mM (at the same Ca/Mg mole ratio) increased the phosphate removal by sedimentation over the pH range from 8 to 10 (compare Runs 1 and 2, Figure 24). A similar increase in carbonate at a constant calcium concentration had no such effect (Figure 25). If enhanced separation were due to increased amounts of $CaCO_3$ in the precipitate, it should not matter how the $CaCO_3$ precipitation was produced -- whether by increasing the initial calcium concentration or the initial carbonate concentration. However, enhanced removals of precipitate were only observed when large initial calcium concentrations were used. It is therefore possible that this enhancement is due to a coagulation phenomenon rather than a "weighting of the precipitate with a dense material. Calcite suspensions carry a net negative charge above pH values of 8 to 9.5 [48] and might well be flocculated by high

concentrations of a positive specie such as Ca^{2+} and uninfluenced by the presence of negatively charged species such as HCO_3^- or CO_3^{2-}.

These preliminary observations on the separation characteristics of calcium phosphate–carbonate suspensions point to the importance of suspension surface properties in the removal of phosphate by precipitation. They also indicate that a fruitful area for investigation exists in the physical characterization of these suspensions to provide information that will lead to effective methods of precipitate separation at pH values below 10.5. At this stage one might conclude that high (>90%) removals of phosphate by calcium phosphate precipitation and sedimentation of solids are only possible at pH values of above 10. To achieve 80% overall phosphate removal at pH values of 10 or lower, the precipitate must be coagulated with a cationic material, and in these experiments it appeared that a large excess calcium dose achieved this objective. It would be better to achieve the same results with lower concentrations of alternative flocculants such as polyelectrolytes or alum or ferric salts which may have both an electrostatic and bridging function.

SECTION X

ACKNOWLEDGMENTS

This investigation was supported in part by Grant No. 17080 DAR from the Environmental Protection Agency. The work was performed by Mr. Arnold B. Menar under the direction of Professor David Jenkins. Mr. Warren Schwartz served as Project Officer for the Environmental Protection Agency. The assistance of Miss Christine Tarr and the late Mr. Philip Palmer performing analyses and conducting experimental work throughout this study is appreciated. The generosity of Mr. Robert Jack for providing X-ray crystallographic facilities is acknowledged. Portions of the experimental phase of this study were conducted with other work performed concurrently on this project. The assistance of Drs. John H. Koon and Larry A. Esvelt in this regard is greatly appreciated.

Preceding page blank

SECTION XI

REFERENCES

1. Nesbitt, J. B., "Phosphate Removal – The State of the Art," J. Water Pollution Control Fed., 41, p. 708 (1969).

2. Menar, A. B., and Jenkins, D., The Fate of Phosphorus in Sewage Treatment Processes. Part II – Mechanism of Enhanced Phosphate Removal by Activated Sludge, SERL Report 68-6, Berkeley Sanit. Eng. Research Lab., University of California (1968).

3. Ferguson, J. F., "The Precipitation of Calcium Phosphates from Fresh Waters and Wastewaters," Ph.D. Dissertation, Stanford University, Stanford, California (1970).

4. Ferguson, J. F., Jenkins, D., and Stumm, W., "Calcium Phosphate Precipitation in Wastewater Treatment," Water - 1970, American Institute of Chemical Engineers.

5. Jenkins, D., Ferguson, J. F., and Menar, A. B., "Chemical Processes for Phosphate Removal," Wastewater Reclamation and Reuse Workshop, Lake Tahoe, California, Proceedings, p. 147 (1970).

6. Rudolfs, W., "Phosphate in Sewage and Sludge Treatment. II. Effect on Coagulation, Clarification and Sludge Volume," Sewage Works J. 19, p. 179 (1947).

7. Wuhrmann, K., "Objective, Technology and Results of Nitrogen and Phosphorus Removal Processes," Advances in Water Quality Improvement, Univ. of Texas Press, p. 21 (1968).

8. Mulbarger, M. C., Grossman III, E., Dean, R. B., Grant, O. L., "Lime Clarification Recovery, Reuse, and Sludge Dewatering Characteristics," J. Water Pollution Control Fed., 41, p. 2070 (1969).

9. Buzzel, J. C., and Sawyer, C. N., "Removal of Algae Nutrient from Raw Wastewater with Lime," J. Water Pollution Control Fed., 39, p. R16 (1967).

10. Seiden, L., and Patel, K., Mathematical Model of Tertiary Treatment by Lime Addition, Report on Contract 14-12-416 between FWQA and General American Research Division (1969).

11. Owen, R., "Removal of Phosphate from Sewage Plant Effluents with Lime," Sewage and Ind. Wastes, 25, p. 548 (1953).

Preceding page blank

12. Spiegel, M., and Forrest, T. H., "Phosphate Removal: Summary of Papers," J. Sanit. Eng. Div., Proc. ASCE, 95 (SA5), pp. 803-827 (1969).

13. Suhr, L. G., Nutrient Removal at Lake Tahoe – Costs and Criteria, report by Cornell, Howland, Hayes, & Merryfield, Engineers and Planners, Corvallis, Oregon (n/d).

14. Culp, R. L., Advanced Wastewater Treatment as Practiced at South Tahoe, Final Report to EPA on R & D Project 17010 ELQ (WRPD 52-01-67) (1971).

15. Garland, C. F., "High Density, Solids Contact," paper presented at FWQA sponsored seminar, Chicago, Ill., June 26-27 (1968).

16. Albertson, O. E., and Sherwood, R. J., "Phosphate Extraction Process," J. Water Pollution Control Fed., 41, p. 1467 (1969).

17. Humenick, M. J., and Kaufman, W. J., "An Integrated Biological-Chemical Process for Municipal Wastewater Treatment," paper presented at the 5th International Water Pollution Research Conference, San Francisco (1970).

18. Stumm, W., and Leckie, J. O., "Phosphate Exchange with Sediments; Its Role in the Productivity of Surface Waters," paper presented at the 5th International Water Pollution Research Conference, San Francisco (1970).

19. Schmidt, L. A., and McKinney, R. E., "Phosphate Removal by a Lime-Biological Treatment Scheme," J. Water Pollution Control Fed., 41, p. 1259 (1969).

20. Ferguson, J. F., Jenkins, D., Eastman, J. D., "Calcium Phosphate Precipitation at Slightly Alkaline pH Values," (in press) J. Water Pollution Control Fed.

21. Vacker, D., Connell, C. H., and Wells, W. N., "Phosphate Removal Through Municipal Wastewater Treatment at San Antonio, Texas," J. Water Pollution Control Fed., 39, p. 750 (1967).

22. Ferguson, J. F., and McCarty, P. L., The Precipitation of Phosphates From Fresh and Waste Waters, Technical Report No. 120, Dept. of Civil Engineering, Stanford University, Stanford, Calif. (1969).

23. Strates, B. S., Neuman, W. F., and Levinskas, G. J., "The Solubility of Bone Mineral. II. Precipitation of Near Neutral Solutions of Calcium and Phosphate," J. Physical Chem., 61, p. 279 (1957).

24. MacGregor, J., and Brown, W. E., "Blood:Bone Equilibrium in Calcium Homeostasis," Nature, 205, p. 359 (1965).

25. Booth, D. H., and Coates, R. V., "The Stability of Calcium Hydrogen Phosphate Precipitated from Solutions of Calcium Nitrate and Phosphoric Acid," J. Chem. Soc., p. 4914 (1961).

26. Walton, A. G., Bodin, W. J., Furedi, H., and Schwartz, A., "Nucleation of Calcium Phosphate from Solution," Canadian J. Chem, 45, p. 2695 (1967).

27. Van Wazer, J. R., Phosphorus and Its Compounds. Volume I, Interscience (1961).

28. Hendricks, S. B., and Hill, W. L., "The Nature of Bone and Phosphate Rock," Proceedings National Academy of Science of US, 36, p. 731 (1950).

29. Rootare, H. M., Deitz, V. P., and Carpenter, F. G., "Solubility Product Phenomena in Hydroxyapatite-Water Systems," J. Colloid Sci., 17, p. 179 (1962).

30. McConnell, D., "Crystal Chemistry of Hydroxyapatite — Its Relation to Bone Mineral," Arch. Oral Biol., 10, p. 421 (1965).

31. Berry, E. E., "The Structure and Composition of Some Calcium-Deficient Apatites," J. Inorg. Nucl. Chem., 29, p. 317 (1967).

32. Eanes, E. D., Gillessen, I. H., and Posner, A. S., "Mechanism of Conversion of Non-Crystalline Calcium Phosphate to Hydroxyapatite," Proceedings International Conference on Crystal Growth, New York (1967).

33. Stumm, W., and Morgan, J. J., Aquatic Chemistry, Wiley-Interscience (1970).

34. Newesely, H., "Changes in Crystal Types of Low Solubility Calcium Phosphates in the Presence of Accompanying Ions," Arch. Oral Biol., Special Supplement, 6, p. 174 (1961).

35. Mooney, R. W., and Aia, M. A., "Alkaline Earth Phosphates," Chem. Rev., p. 433 (1961).

36. Chave, K. E., Deffeyes, K. S., Weyl, P. K., Garrels, R. M., and Thompson, M. E., "Observations on the Solubility of Skeletal Carbonates in Aqueous Solutions," Science, 137, p. 33 (1962).

37. Simpson, D. R., "Apatite and Octa-Calcium Phosphate: Effects of Carbon Dioxide and Halogens on Formation," Science, 154, p. 1660 (1966).

38. Somasundaran, P., "Zeta Potential of Apatite in Aqueous Solutions and Its Change During Equilibration," J. Colloid and Interface Sci., 27, p. 659 (1968).

39. Parks, G. A., "The Isoelectric Points of Solid Oxides, Solid Hydroxides, and Aqueous Hydroxo Complex Systems," Chem. Rev., 65, p. 177 (1965).

40. LaMer, V. K., and Smellie, R. H., "Flocculation, Subsidence and Filtration of Phosphate Slimes," J. Colloid Sci., 11, p. 704 (1956).

41. American Public Health Association, Standard Methods for the Examination of Water and Wastewater, 11th Edition (1960) and 10th Edition (1955).

42. FWPCA Methods for Chemical Analysis of Water and Wastes, Federal Water Quality Administration, Cincinnati, Ohio (1969).

43. Jenkins, D., Analytical Methods, Berkeley: Sanit. Eng. Research Lab., University of California (1966).

44. Winneberger, J. H., Austin, J. H., and Klett, C. A., "Membrane Filter Weight Determinations," J. Water Pollution Control Fed., 35, p. 807, (1963).

45. Basset Jr., H., "Beitrage zum Studium der Calciumphosphate," Z. Anorg. Chemie, 59, p. 1 (1908).

46. Bard, A. J., Chemical Equilibrium, Harper and Row, New York (1966).

47. Sillen, L. G., and Martell, A. E., Stability Constants of Metal-Ion Complexes, London Chem. Soc., Special Publication No. 17 (1964).

48. Somasundaran, P., and Agar, G. E., "The Zero Point of Change of Calcite," J. Colloid and Interface Sci., 24, p. 433 (1967).

SECTION XII

GLOSSARY

Symbol	Definition
$[Ca^{2+}]_{in}$	Influent calcium ion concentration
$[Ca^{2+}]_{ss}$	Steady state calcium ion concentration
$[Ca_T]$	Total dissolved calcium concentration
CSTR	Continuously stirred tank reactor
C_T	Total carbon = $H_2CO_3 + HCO_3^- + CO_3^{2-}$
DCP	Dicalcium phosphate
HAP	Hydroxyapatite
hp	Horsepower
k_1	First equilibrium constant of phosphoric acid
k_2	Second equilibrium constant of phosphoric acid
k_3	Third equilibrium constant of phosphoric acid
ℓ	liter
$Mg(OH)_2$	Magnesium hydroxide
mg/ℓ	milligram per liter
nm	nanometers
OCP	Octacalcium phosphate
P_{in}	Influent phosphate concentration
$[PO_4^{3-}]_{ss}$	Steady state PO_4^{3-} concentration
P_{ss}	Steady state phosphate concentration
P_T	Total orthophosphate = $H_3PO_4 + H_2PO_4^- + HPO_4^{2-} + PO_4^{3-}$
PVC	Polyvinyl chloride

Symbol	Definition
pA	Negative logarithm of a solubility product
pH_{zpc}	pH of zero point of charge
sec^{-1}	Reciprocal seconds
SERL	Sanitary Engineering Research Laboratory
TCP	Tricalcium phosphate
zpc	Zero point of charge
μ	Micron

SECTION XIII

APPENDICES

		Page
A.	Walton Technique for Determining Stoichiometry of Nucleating Solid Phase	81
B.	Example of Manual Computation of Residual Phosphate Values	85
C.	Daily Wastewater Experimental Data	89

APPENDIX A

WALTON TECHNIQUE FOR DETERMINING STOICHIOMETRY OF NUCLEATING SOLID PHASE [26]

Preceding page blank

Walton et al. [26] state that the energy barrier to nucleation, ΔG° (nucleation) is given by the following expression:

$$\Delta G^{\circ} \text{ (nucleation)} = \Delta G^{\circ} \text{ (cluster)} - \Delta G^{\circ}sp \text{ (solubility)} \quad . \quad (12)$$

The terms on the right-hand side of Equation (12) can be evaluated as follows: The standard free energy of the cluster, ΔG° (cluster), depends on the type and number of interacting ionic species. In general, if ionic specie A^{a+} interacts with ionic specie B^{b-} to form a neutral ionic aggregate, the metastable equilibrium is given by the equation:

$$xbA^{a+} + xaB^{b-} \rightleftharpoons (Ab^{a+}Ba^{b-})_x \quad . \quad (13)$$

The condition for equilibrium is $\Delta G_{x_o} = 0$, or

$$\Delta G_{x_o} = bx\mu_A + ax\mu_B - x\mu_{AB} - \Sigma\sigma_{ij} = 0 \quad (14)$$

where:

μ_A, μ_B, and μ_{AB} are the chemical potentials of species A^{a+}, B^{b-}, and $(A_b^{a+} B_a^{b-})_x$, respectively,

σ_{ij} is the interfacial energy of the interface between the i and j phases.

After equating $\mu_{AB} = \mu^{\circ}_{AB}$ (solid), Walton defines the total standard energy of the critical cluster $\Delta G^{\circ}_{x_o}$ as:

$$\Delta G^{\circ}_{x_o} \text{ (cluster)} = -RT \ln[A]^b[B]^a + \Sigma \frac{\sigma_{ij}}{x} \quad . \quad (15)$$

Also

$$\Delta G^{\circ}_{sp} \text{ (solubility)} = -RT \ln K_{sp} \quad (16)$$

where K_{sp} is the solubility product.

Now, substituting Equations (15) and (16) in Equation (12) we obtain Equation (17):

$$\Delta G^{\circ}\ (\text{nucleation}) = -RT\ \ln[A]^{b}[B]^{a} + \Sigma\ \frac{\sigma_{ij}}{x} - RT\ \ln K_{sp} \quad . \qquad (17)$$

Rearranging Equation (17)

$$\ln[A]^{b}[B]^{a} = \Sigma\ \frac{\sigma_{ij}}{xRT} + \ln K_{sp} - \frac{\Delta G^{\circ}\ (\text{nucleation})}{RT} \quad . \qquad (18)$$

The right-hand side of Equation (18) is constant at constant temperature for any one critical size nucleus of constant composition and interfacial energy. Thus:

$$\ln[A] = -\frac{a}{b}\ \ln[B] + \text{constant} \quad . \qquad (19)$$

Thus, if the above criteria hold, a plot of the logarithm of the critical concentration of the cation A against that of the anion B should yield a straight line. The slope of this line gives the stoichiometric ratio of the initial phase.

The above derivation does not depend upon the detailed nature of the nucleation process and similar reasoning can be applied to systems in which the nucleus contains more than two ionic species.

Walton and coworkers [26] visualize the formation of a critical nucleus and the beginning of calcium phosphate precipitation as follows:

$$\begin{array}{c} ax\ H_3PO_4 + bx\ Ca(OH)_2 + x\ (c - 2b)\ H_2O \\ \updownarrow \\ [Ca_bH_{3a-2b}(PO_4)_{3c}\ H_2O]x \quad \text{(critical nucleus)} \\ \downarrow \\ \text{precipitation} \end{array} \qquad (20)$$

At the onset of nucleation, the relation between the concentrations of the species is given by Equation (20) i.e.,

$$\log\left([Ca^{2+}][OH^{-}]^{2}\right)^{b}\ \left([H^{+}][H_2PO_4^{-}]\right)^{a} = \text{constant} \quad . \qquad (21)$$

Equation (21) could be rearranged

$$b\ \log\left([Ca^{2+}][OH^{-}]^{2}\right) + a\ \log\left([H^{+}][H_2PO_4^{-}]\right) = \text{constant} \qquad (22)$$

$$\log\left([Ca^{2+}][OH^{-}]^{2}\right) = -\left(\frac{a}{b}\right)\ \log\left([H^{+}][H_2PO_4^{-}]\right) + \text{constant} \qquad (23)$$

Thus if log ($[Ca^{++}][OH^-]^2$) is plotted against log ($[H^+][H_2PO_4^-]$) for a series of experiments, a straight line should result with a slope of a/b that gives the ratio of phosphate to calcium in the nucleating or steady state phase. Data from Walton et al. [26], together with data from the chemically-defined systems of this work, are presented in Figure 26. The data from the chemically-defined systems appear in the text of this report (Figure 9) on a somewhat more expanded scale.

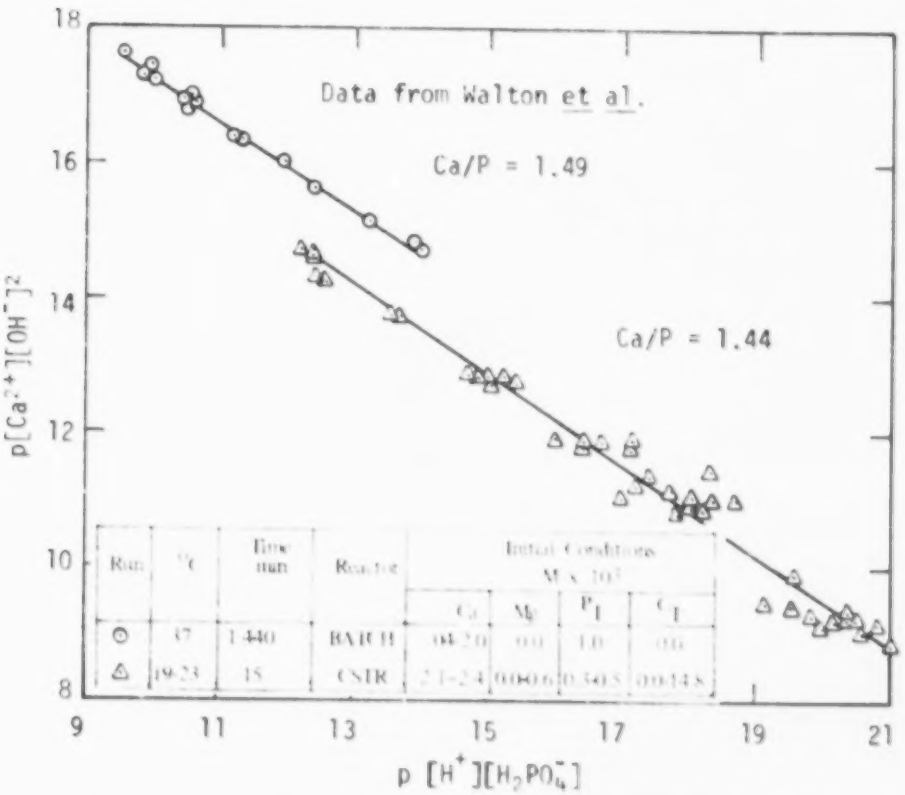


FIGURE 26. CRITICAL IONIC CONCENTRATIONS AS DETERMINED BY WALTON et al. AND BY THIS INVESTIGATION

APPENDIX B

EXAMPLE OF MANUAL COMPUTATION OF RESIDUAL PHOSPHATE VALUES

In this presentation the manual computation of residual dissolved phosphate concentrations will be illustrated by the following example:

Initial Conditions: Ca, 2.19 mM; P_T, 0.38 mM; Mg, 0.59 mM; C_T, 5.95 mM.

Conditions of Precipitation: pH 10.

Predictive Equation:

$$3 \log\{[Ca^{2+}]_{in} - 1.5\,[P_{in} - P_{ss}]\} + 2 \log[PO_4^{3-}] = -23.56 \qquad (10)$$

Equation (10) is solved for P_{ss} by trial and error. Thus, assume $[P_{in} - P_{ss}] = 0.9\,P_{in}$, i.e., $P_{ss} = 3.8 \times 10^{-5}$M. Now, compute

$$[Ca^{2+}]_{ss} = (2.19 - 0.9) \times 1.5 \times 0.38 \times 10^{-3}$$
$$= 1.68 \times 10^{-3}\text{M} \quad .$$

Substituting this value for $[Ca^{2+}]_{ss}$ in Equation (10) and solving for $[PO_4^{3-}]_{ss}$ yields:

$$[PO_4^{3-}]_{ss} = 2.34 \times 10^{-8}\text{M} \quad .$$

The fraction that $[PO_4^{3-}]_{ss}$ is of P_{ss} at any pH can be computed from equilibrium constants of phosphoric acid and $[H^+]$.

Thus,

$$P_{ss} = 4.9 \times 10^{-6}\text{M} \quad .$$

This value of P_{ss} is not within 5% of the assumed P_{ss} value. Therefore, the computation is repeated using,

$$P_{ss} = 4.9 \times 10^{-6}\text{M} \quad .$$

This yields

$$P_{ss} = 5.26 \times 10^{-6}\text{M}.$$

The difference between this value and the assumed value is again greater than 5% so that a third iteration is necessary using,

$$P_{ss} = 5.26 \times 10^{-6} M \quad .$$

The computation now yields

$$P_{ss} = 5.26 \times 10^{-6} M$$

an identical value to that assumed.

The computation of residual dissolved phosphate from Equation (10) can be modified when necessary to account for the calcium that is required to precipitate calcium carbonate. The solubility product chosen for calcium carbonate was

$$[Ca^{2+}][CO_3^{2-}] = 2.6 \times 10^{-9} \qquad (24)$$

a value typical of a destabilized calcium carbonate formed under the precipitation conditions encountered in wastewater precipitation processes [10,22].

Now, setting the $[Ca^{2+}]$ incorporated into calcium carbonate precipitate equal to x, we have

$$[Ca^{2+} - x][CO_3^{2-} - x] = 2.6 \times 10^{-9} \quad . \qquad (25)$$

This quadratic equation can be solved and the amount of calcium removed as calcium carbonate precipitate determined.

Additional corrections for the complexation of calcium become significant at pH values of greater than pH 10. The various complexes of calcium can be regarded as removing the calcium from the sphere of activity in precipitating phosphate. The complexes considered were: $CaOH^+$, $CaCO_3(aq)$, $CaHCO_3^+$, and $CaPO_4^-$. Thus,

$$[Ca_T] = [Ca^{2+}] + [CaOH^+] + [CaCO_3(aq)] + [CaHCO_3^+] + [CaPO_4^-] \qquad (26)$$

where $[Ca_T]$ is the total dissolved calcium concentration. The equilibrium constants for these complexes are as follows:

$Ca^{2+} + OH^- = CaOH^+$	$K_{CaOH^+} = 23.5$
$Ca^{2+} + CO_3^{2-} = CaCO_3(aq)$	$K_{CaCO_3(aq)} = 1.59 \times 10^3$
$Ca^{2+} + HCO_3^- = CaHCO_3^+$	$K_{CaHCO_3^+} = 18.2$
$Ca^{2+} + PO_4^{3-} = CaPO_4^-$	$K_{CaPO_4^-} = 2.89 \times 10^{+6}$

From the mass balance equation for total dissolved calcium, Equation (26), and the equilibrium constants for calcium complexes the following expression for $[Ca^{2+}]$ is obtained:

$$[Ca^{2+}] = \frac{[Ca_T]}{1 + K_{CaOH^+}[OH^-] + K_{CaCO_3(aq)}[CO_3^{2-}] + K_{CaHCO_3^+}[HCO_3^-] + K_{CaPO_4^-}[PO_4^{3-}]} \quad (27)$$

The most significant terms in this equation are those for the $CaCO_3(aq)$ and $CaPO_4^-$ complexes. The $CaOH^+$ and $CaHCO_3^+$ complexes can be neglected at pH values below 11. Thus a simplified form of Equation (27) can be used

$$[Ca^{2+}] = \frac{[Ca_T]}{1 + K_{CaCO_3(aq)}[CO_3^{2-}] + K_{CaPO_4^-}[PO_4^{3-}]} \quad (28)$$

For the ranges of concentrations and pH conditions in the experiments conducted here, neglecting the $CaPO_4^-$ complex, would introduce an error of 5-10% in values of $[Ca^{2+}]$. Thus Equation (28) could be further simplified to

$$[Ca^{2+}] = \frac{[Ca_T]}{1 + K_{CaCO_3(aq)}[CO_3^{2-}]} \quad (29)$$

Computation of the initial $[Ca^{2+}]$ available for precipitating calcium phosphate, therefore, consists of calculating the amount of calcium removed by calcium carbonate precipitation and then converting the residual dissolved calcium value to $[Ca^{2+}]$ by correcting for calcium complexes by one of the Equations (27, 28, or 29).

APPENDIX C

DAILY WASTEWATER EXPERIMENTAL DATA

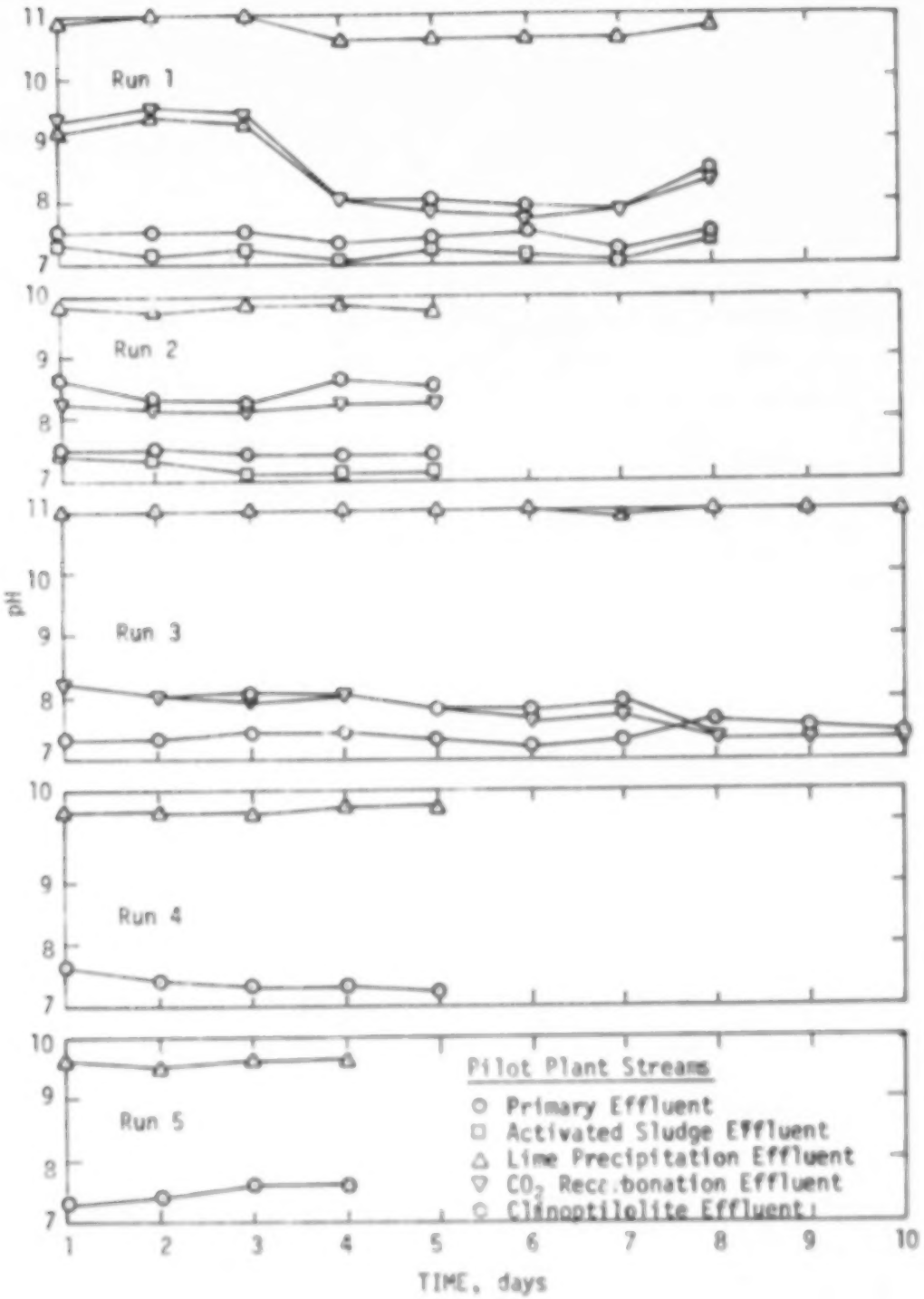


FIGURE 27. EFFECT OF UNIT PROCESSES ON pH

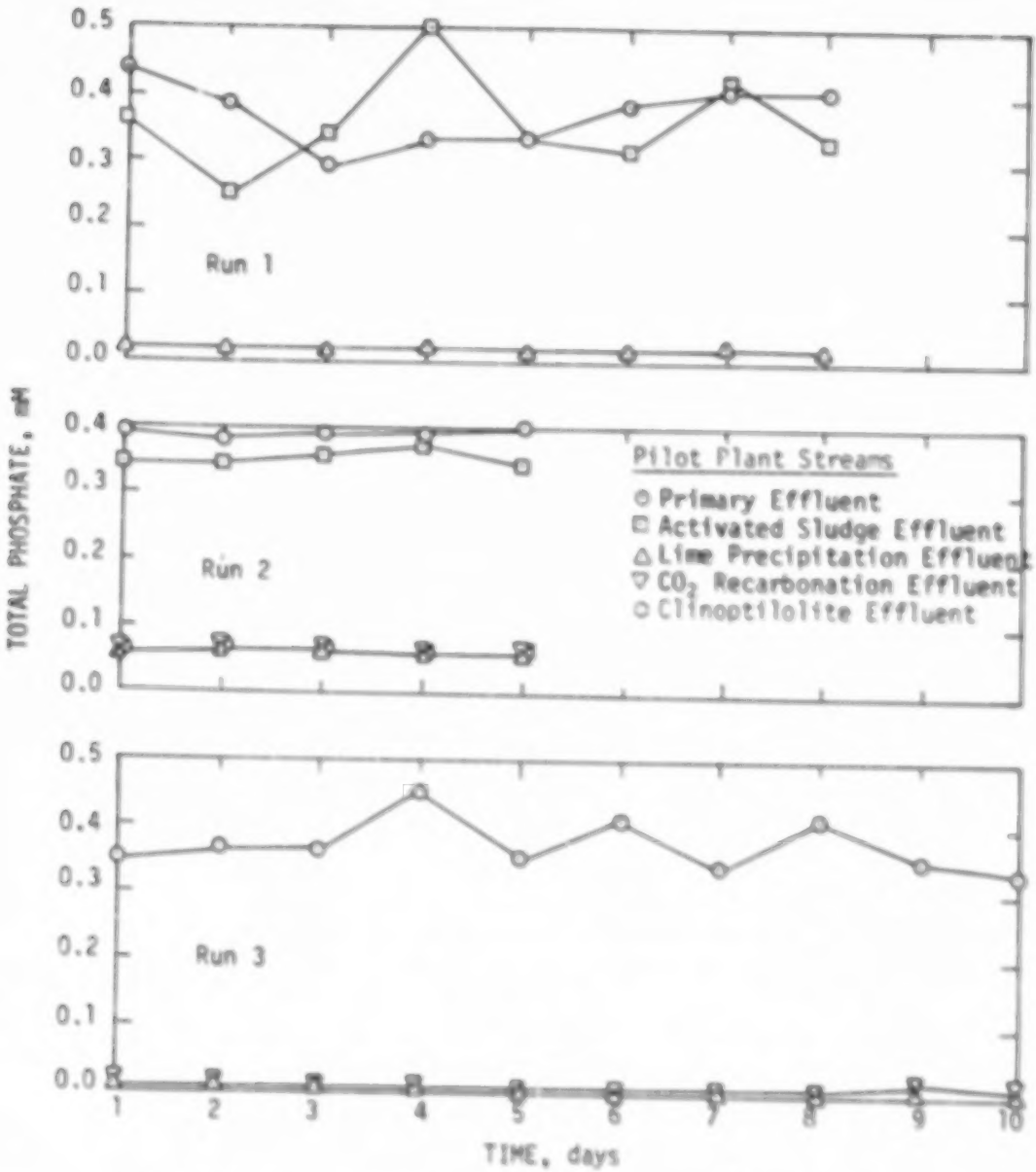


FIGURE 28. EFFECT OF UNIT PROCESSES ON TOTAL PHOSPHATE RESIDUALS (RUNS 1, 2 AND 3)

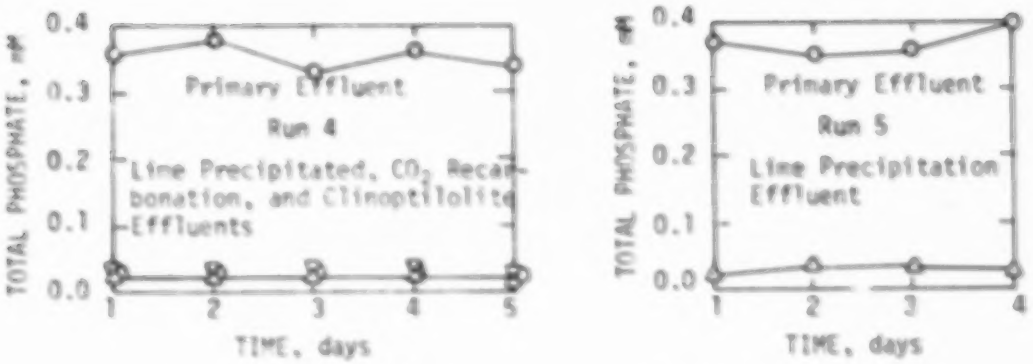
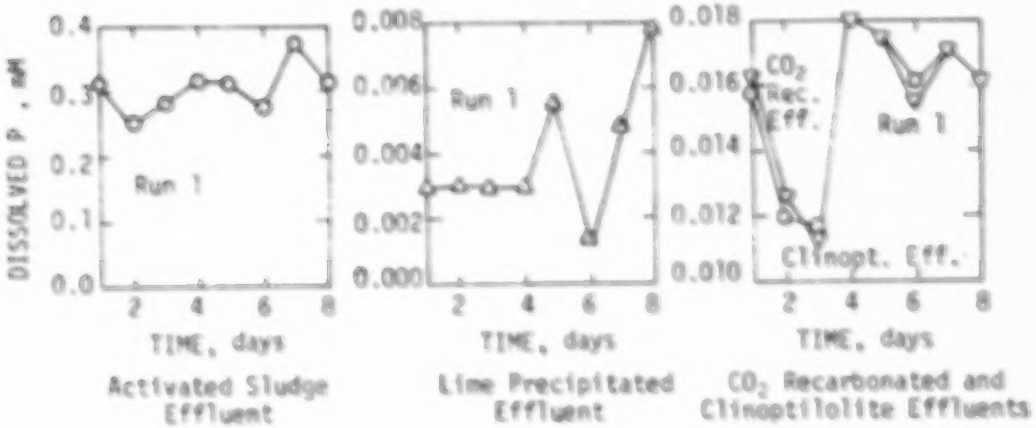


FIGURE 29. EFFECT OF UNIT PROCESSES ON TOTAL PHOSPHATE RESIDUALS (RUNS 4 AND 5)



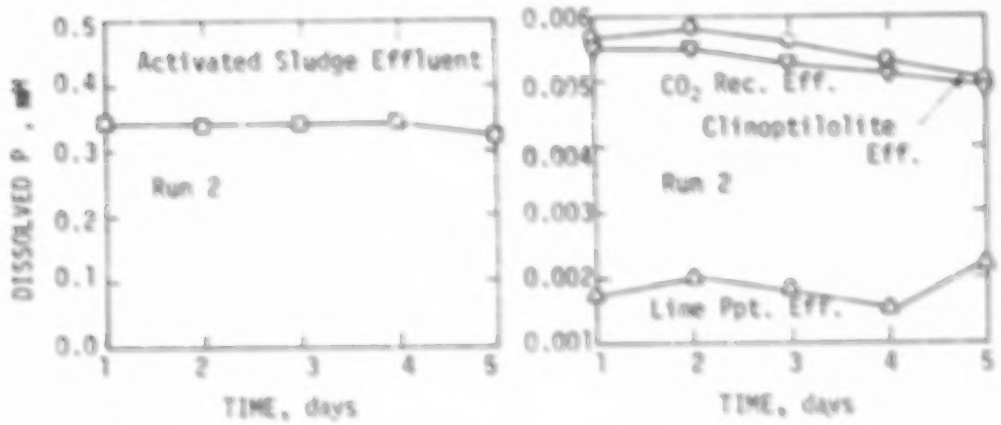


FIGURE 30. EFFECT OF UNIT PROCESSES ON DISSOLVED PHOSPHATE RESIDUALS (RUNS 1 AND 2)

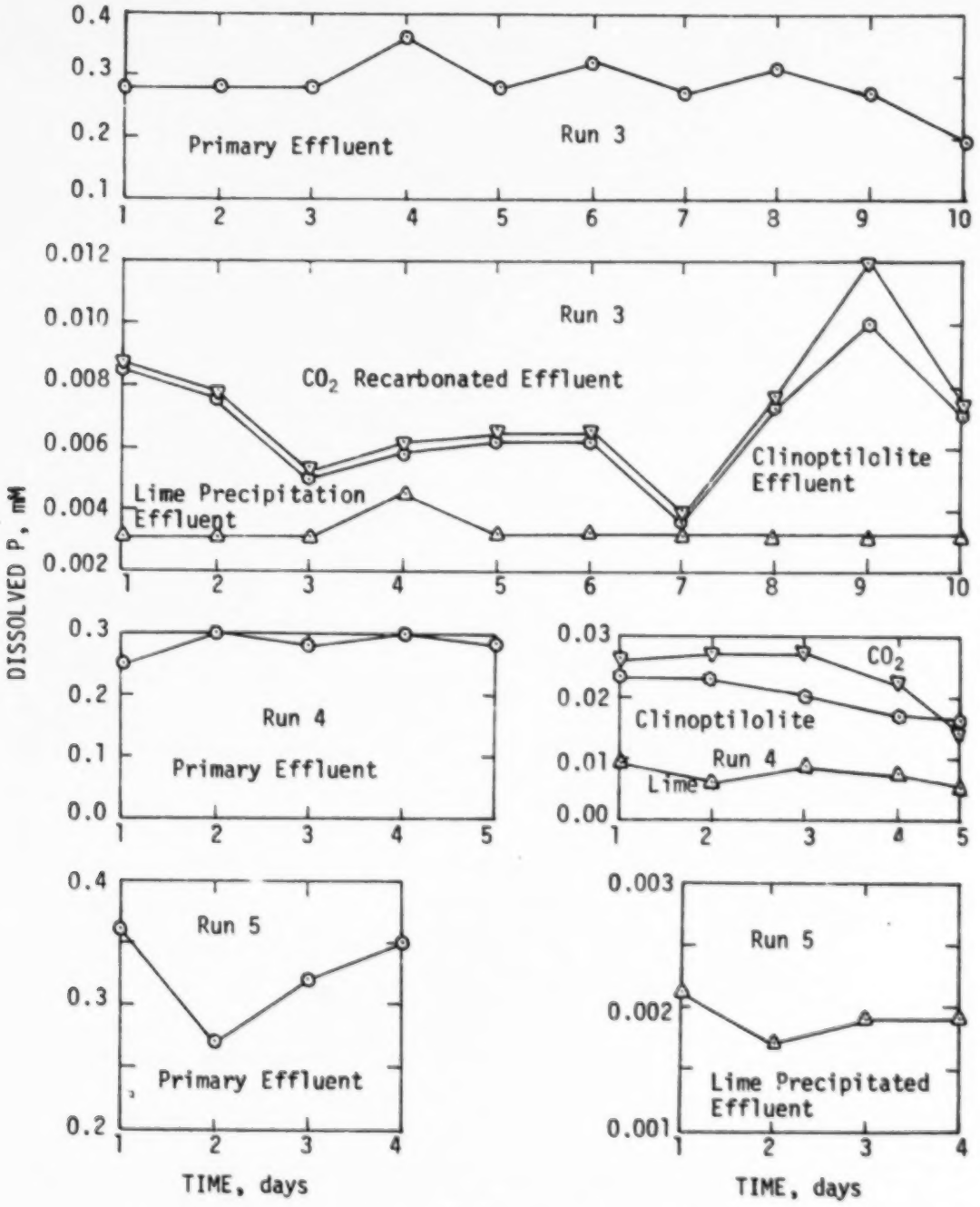


FIGURE 31. EFFECT OF UNIT PROCESSES ON DISSOLVED PHOSPHATE RESIDUALS (RUNS 3, 4 AND 5)

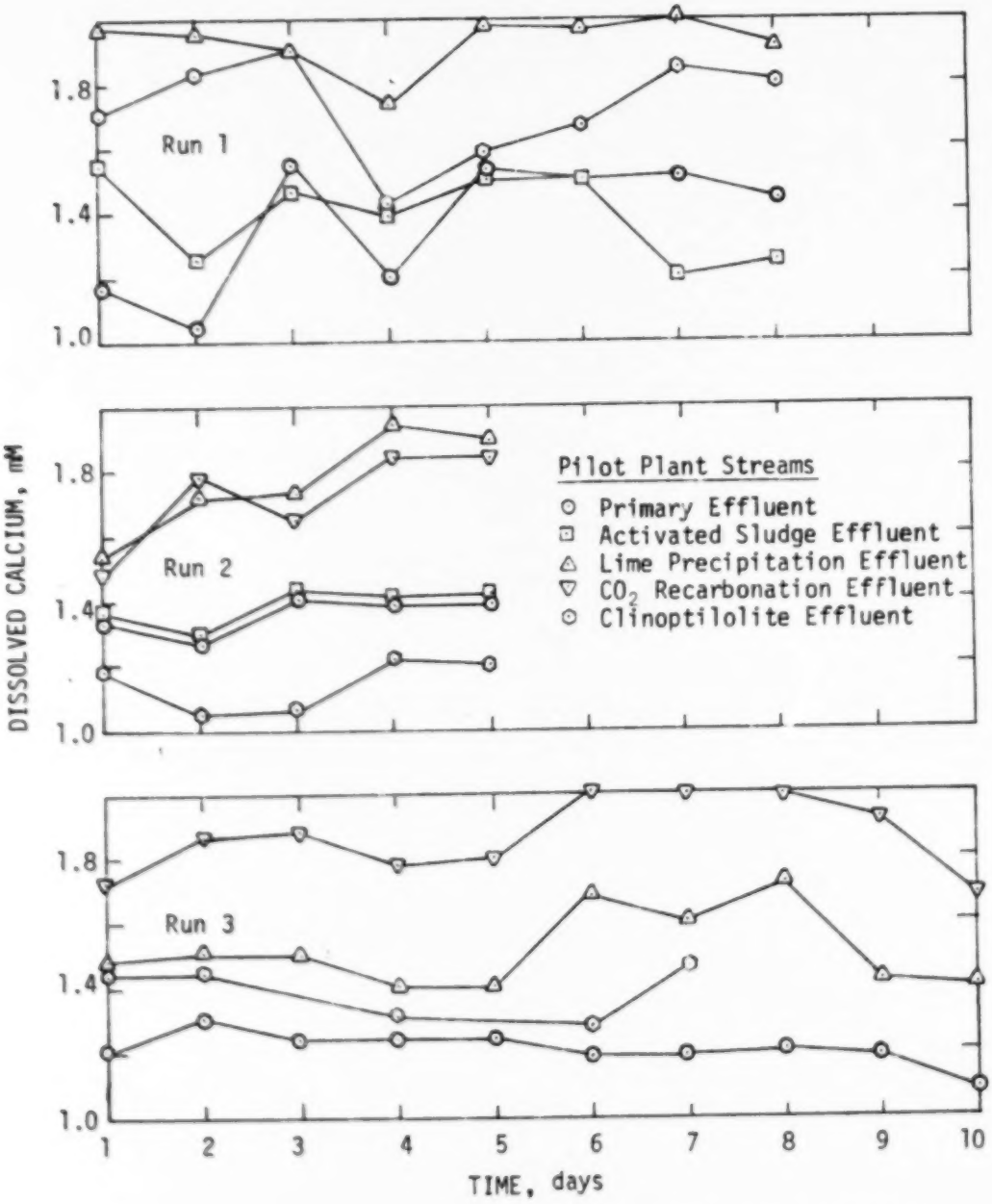


FIGURE 32. EFFECT OF UNIT PROCESSES ON DISSOLVED CALCIUM CONCENTRATION (RUNS 1, 2 AND 3)

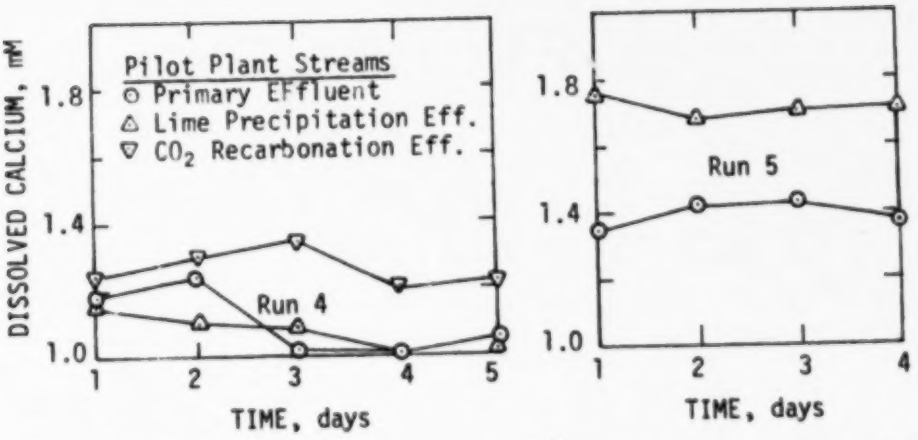


FIGURE 33. EFFECT OF UNIT PROCESSES ON DISSOLVED CALCIUM CONCENTRATION (RUNS 4 AND 5)

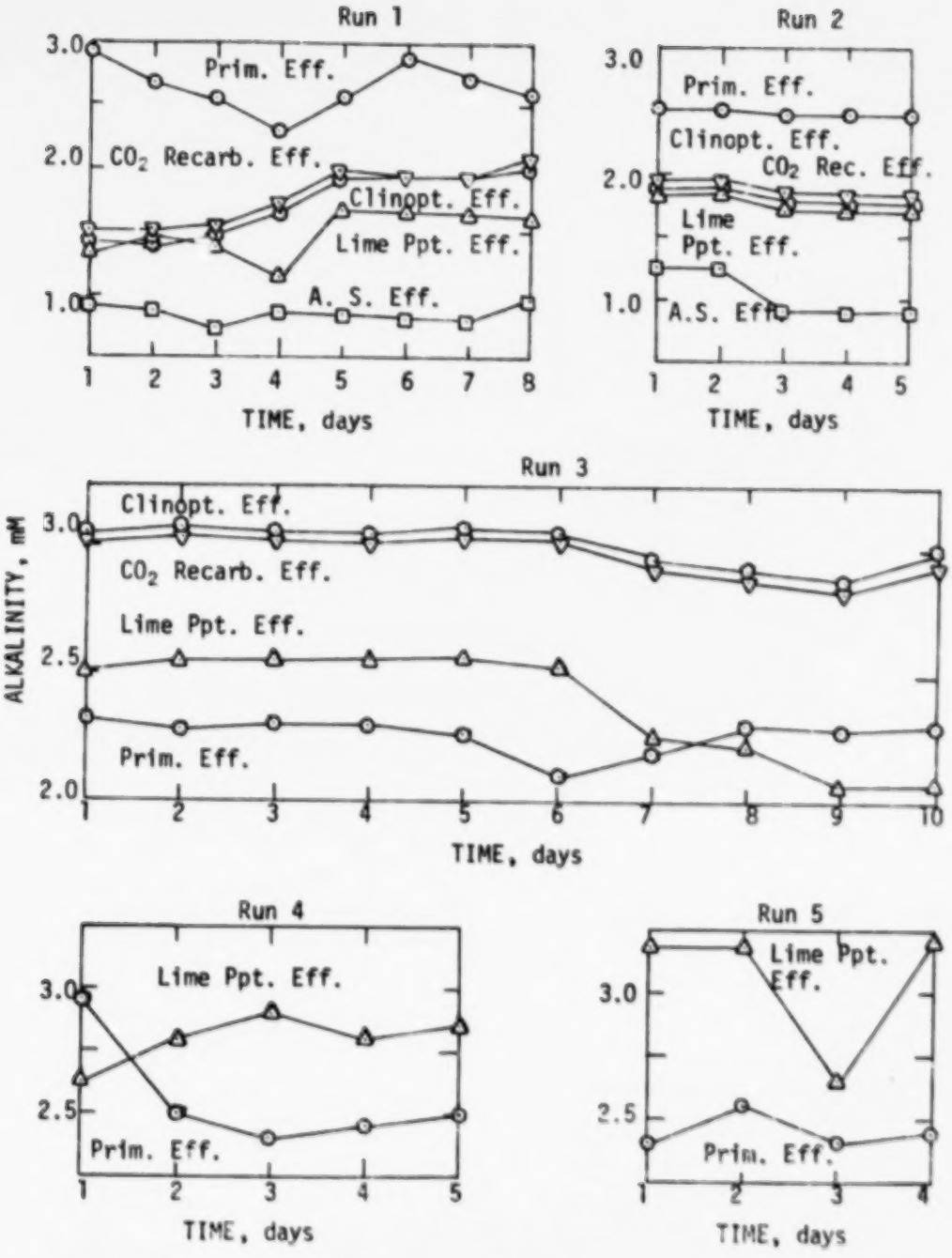


FIGURE 34. EFFECT OF UNIT PROCESSES ON ALKALINITY

SELECTED WATER RESOURCES ABSTRACTS INPUT TRANSACTION FORM	1 Report No.	2 W
Calcium Phosphate Precipitation in Wastewater Treatment		5. Report Date 6. June 1972 8. Performing Organization Report No. SERL 72-6
Menar, Arnold B. and Jenkins, David		
California University Sanitary Engineering Research Laboratory		EPA WQO 17080 DAR
12. Sponsoring Organization		13. Type of Report and Period Covered

Environmental Protection Agency report number, EPA-R2-72-064, December 1972.

This investigation examined the precipitation of calcium phosphate both from chemically-defined solutions representative of wastewater composition and from wastewater. The steady state solid phase that controlled dissolved phosphate residual was an amorphous tricalcium phosphate. The solubility of this phase, determined from chemically-defined systems, was used with success to predict dissolved phosphate residuals from both chemically-defined systems and wastewaters. Suspension recycle was found to result in lower dissolved phosphate residuals, but poor suspension settling below pH 10 made this process difficult to maintain. Suspension settling was enhanced by $Mg(OH)_2$ precipitation but not by $CaCO_3$ precipitation. In wastewater of moderate alkalinity and hardness, a phosphate removal in excess of 80% was consistently achieved at pH 9.5 with lime doses of, at the most, 200 mg/liter as $CaCO_3$. The overall phosphate removal performance was dictated by the performance of the precipitation reactor and its ensuing sedimentation basin. Phosphate-containing particles that escaped sedimentation could not be removed by filtration because they dissolved rapidly during the recarbonation process that necessarily precedes the filtration step.

17a. Descriptors

* Waste Treatment — Sewage Treatment

17b. Identifiers

Calcium phosphate, Tricalcium phosphate, Calcium carbonate, Calcite, Magnesium hydroxide

17c. COSATI Field/Group 05D

19. Security Class (Report)	21. No. of Pages	Send To:
20. Security Class (Page)	22. Price	WATER RESOURCES SCIENTIFIC INFORMATION CENTER U.S. DEPARTMENT OF THE INTERIOR WASHINGTON, D.C. 20240

D. Jenkins	California University

U.S. GOVERNMENT PRINTING OFFICE